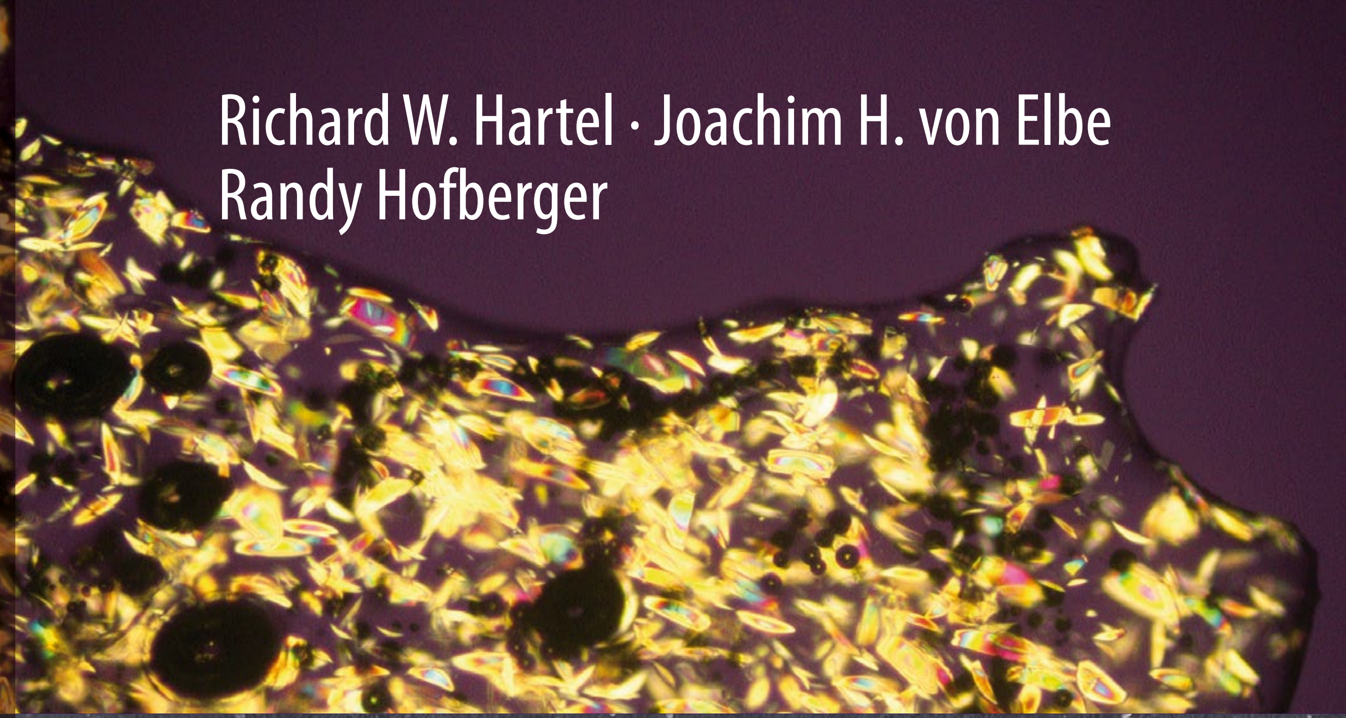

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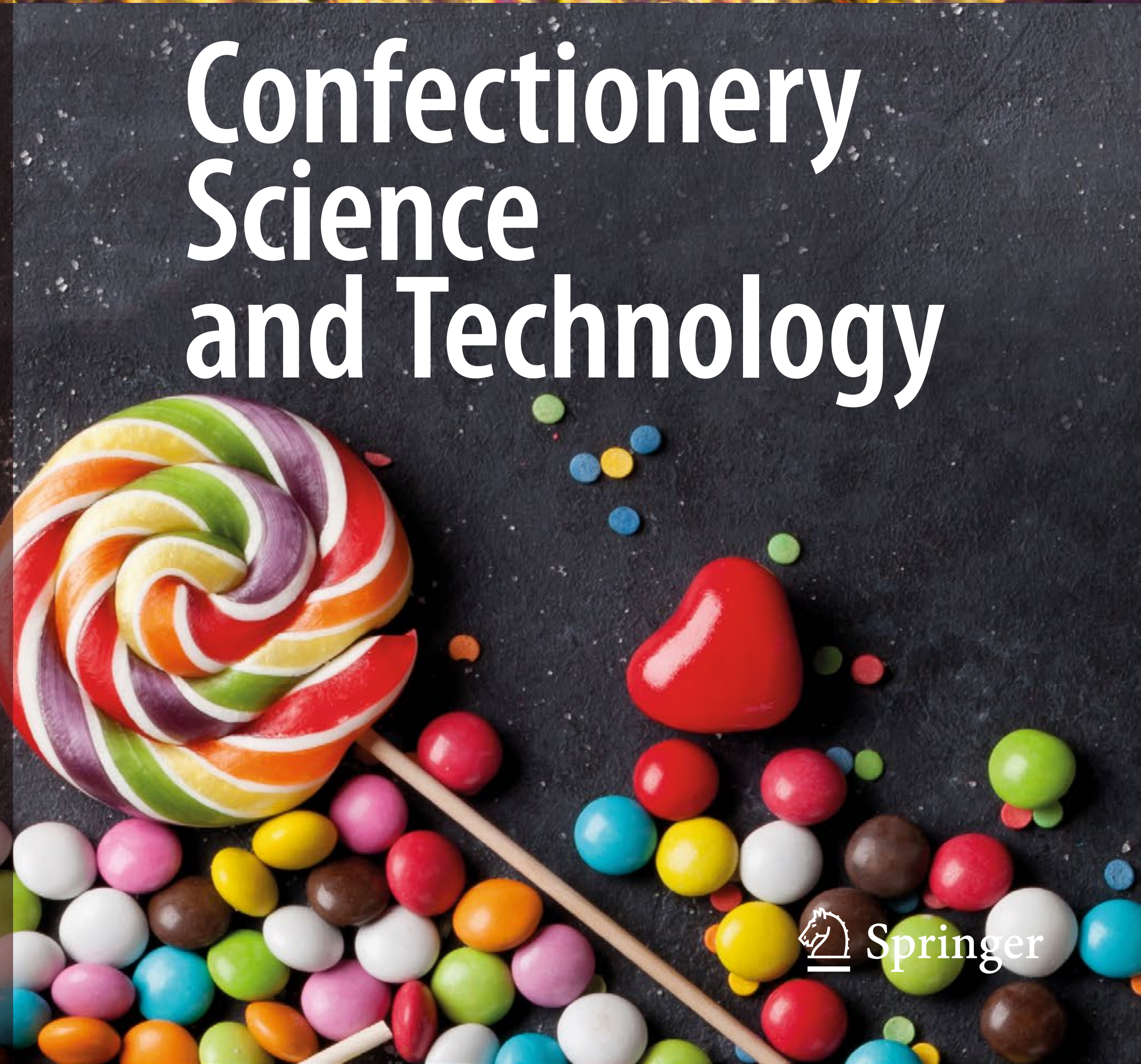

Confectionery Science and Technology

Springer

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Preface

In the summer of 1963, the National Confectioners' Association (NCA) decided to conduct a "candy school", or Resident Course in Confectionery Science, at the University of Wisconsin-Madison. Fifty-five years later, candy school is still going strong, having been led by only two UW-Madison course directors – Dr. Joe von Elbe (1963–1997) and Dr. Rich Hartel (1998-current). Although the course is now run solely by UW-Madison, without the assistance of NCA, it has maintained a preeminent status throughout the candy industry in the United States, and even beyond.

Candy school is a unique collaboration between the candy industry and UW-Madison. Experienced industry instructors work with UW-Madison faculty to provide both the practical application and the scientific basis of candy making. Each day of the course, one, two, or sometimes three, new instructors, all considered to be experts in their area, travel to Madison to impart their knowledge to the next generation of candy technologists. Each instructor first presents a lecture on the candy category of the day, and then leads a practical lab section. These labs are designed to document how ingredients and processing conditions mutually influence candy qualities, the primary objective of candy school. Since failure is often the best learning tool, some of the lab conditions are designed to "fail".

With these dedicated industry professionals teaching practical candy making, thirty attendees each year gain practical expertise across a broad range of candy categories. Covering everything from hard candy to chocolate in two weeks, attendees are quickly and completely immersed in candy science and technology. Over the years, more and more science has been injected into candy school as our knowledge of the basic principles of candy-making come to light through research.

In 2003, the Food Science Department at UW-Madison began offering a 3-credit senior level course on candy science. Modeled after the summer candy school, students are led through candy school material throughout the semester. A new candy category is covered each week, from hard candy through chocolate. The primary difference between this course and candy school is that it is more of an academic course, as would be expected for BS Food Science graduates. However, these students also get much of the practical candy-making expertise as well.

This book is the culmination of over a decade of trying to bring these courses to everyone, not just those who can afford the two weeks away from work each summer (it used to be a 3-week course for the first 30 years) or a semester at UW-Madison. Loosely modeled after the candy school curriculum, the volume is divided into three different sections. In the first section, the physico-chemical bases of the ingredients used in confections are covered. In candy school, the content in these chapters is dispersed throughout the course as needed (rather than having a day or 2 of science principles to start the course). The second section covers the sugar-based confections, in the general order of increasing complexity, or increasing number of ingredient additions made to the sweetener. Finally, the third section covers fat-based confections, namely chocolate and compound coatings.

In this book, we hope to provide a comprehensive summary of candy science and technology. The candy chapters have been designed to provide useful information for both the novice and professional. The first sections of each chapter, covering ingredients and manufacturing practices, should be accessible to readers of all levels. These are followed by more technical sections on microstructure and the important scientific principles that go into making that candy, material nominally targeted to more technically trained readers. The final sections cover shelf life and trouble shooting, providing guidance for all candy makers.

As noted above, putting together this book has been a long and arduous path for the authors. In many ways, this book has been a mountain to get over, requiring a monumental effort. Fortunately, we have had help all along the way. We could not have made this happen without considerable support from a whole host of people, too numerous to mention individually.

Primary thanks go to each candy school instructor who reviewed the chapter(s) for which they are responsible. They are acknowledged at the end of each chapter. Various UW-Madison students have been enlisted over the years to help with book preparation, from literature review to figure construction. Although all merit recognition, one student in particular stands out for her contributions to the figures found throughout the book – Sarah Vogel. Her assistance over the past five years to bring a professional touch to the figures has been an enormous help to get us over this book project mountain.

Finally, we especially acknowledge the entire candy industry for supporting the program, without which this book would not have been possible.

For those who haven't yet been to candy school, we hope this book serves to whet your appetite to learn more by attending our two-week course. For those who have been to candy school, we hope this book supplements those huge course notebooks you had to carry (or ship) home.

Madison, WI, USA Richard W. Hartel
Madison, WI, USA Joachim H. von Elbe
Burlington, WI, USA Randy Hofberger
April 2017

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About the Authors

Richard W. Hartel PhD has been a Professor of Food Engineering with the Department of Food Science at the University of Wisconsin-Madison since 1986. He conducts research on phase transitions in foods, primarily sugar confections, chocolate and ice cream. He teaches courses in Food Manufacturing, Food Preservation, Food Functionality, and Candy Science, as well as a freshman career orientation course. He has been involved with the UW Resident Course in Confectionery Technology (candy school) as an instructor since 1987 and as lead coordinator since 1998.

Joachim H. von Elbe PhD Is Professor and Chairman Emeritus with the Department of Food Science at the University of Wisconsin. He served for 38 years teaching courses in food chemistry with emphasis on plant pigments, their use as food and pharmaceutical colorants, and color and texture changes in canned vegetables. In 1963 he introduced, with cooperation with the confectionery industry, a three week candy technology course designed specifi cally for people in the industry. Since that time the course has been taught annually, and is now known as the UW Resident Course in Confectionery Technology.

Randall (Randy) Hofberger is the principle of R & D Candy Consultants LLC. Previously he had a long career at Nestle Confections USA in technical applications with an emphasis on caramels and chocolates. He has been an instructor at various confectionery courses including UW Resident Course in Confectionery Technology (candy school) and Retail Confectioners International (RCI).

Abbreviations

CMC	Critical micelle concentration
DAG	Diacylglycerol, or diglyceride
DSC	Differential scanning calorimeter
FFA	Free fatty acid
HLB	Hydrophilic-lipophilic balance
MAG	Monoacylglycerol, or monoglyceride
NMR	Nuclear magnetic resonance
PGPR	Polyglycerol polyricinoleate
SFC	Solid fat content
SFI	Solid fat index
TAG	Triacylglycerol, or triglyceride

Part I

Ingredient Chemistry and Functionality

Chemistry of Bulk Sweeteners

1

Sweeteners are the primary ingredients in the manufacture of confections. Chemically, the primary sweeteners in confections are carbohydrates, which consist of a group of widely varied chemical substances present in both plants and animals. For example, in dry corn, approximately 55% of the solids are carbohydrates. The word "carbohydrates" itself means hydrated carbon. Thus, carbohydrate chemistry mostly deals with chains of carbon atoms hydrated with water, with a general formula of $C_x(H_2O)_y$.

Although only three atoms are involved, the chemistry of sweeteners can be very complex. Variations such as carbon chain length and branching, among others, allow for the existence of numerous combinations of the three atoms that provide the range of chemical characteristics of carbohydrates. The main groups of interest for confectionery manufacture are monosaccharides (e.g., glucose and fructose), oligosaccharides (e.g., the disaccharides including sucrose, maltose, and lactose, and starch hydrolysates), and polysaccharides (e.g., starches). Oligosaccharides are carbohydrates consisting of 2–20 monosaccharide units joined by glycosidic linkages. Compounds containing three saccharides are trisaccharides, while four to ten are tetra-, penta-, hexa-, hepta-, octa-, nona-, decasaccharides, respectively. Various oligo- and polysaccharide products are used in confections. However, sweetening power generally decreases as carbon chain length increases (although other factors affect sweetness as well). Most confections contain primarily smaller saccharides, but with a balance of oligosaccharides for functional properties (i.e., control of crystallization).

A wide range of sweeteners is used in the manufacturing of confections and chocolates, with the most common being cane or beet sugar (sucrose), glucose (corn) syrup, high fructose syrup, liquid sugar (67% sucrose dissolved in water), and invert sugar, the hydrolysis product of sucrose. Sugar alcohols (or polyols) are used for "diabetic" candies since they induce no insulin response. High intensity sweeteners are used to enhance sweetness, particularly when sugar alcohols are used.

The original candies probably were sweetened naturally, with materials like honey and maple syrup. As sucrose became more available, confectioners began using it as the primary sweetener in confections, with its hydrolysis product, invert sugar, used as the first doctoring agent (to control crystallization). As the sweetener industry matured, more and more different types of sweeteners have become available that provide excellent control for the confectioner. Knowledge of the physical and chemical properties of carbohydrates has made it possible for the confectionery industry to develop the many products available on the market today.

Sweeteners, beyond providing sweetness to confections, play an important role in determining the texture. Crystallization of sucrose in some products is encouraged, while in others, complex carbohydrates such as glucose (corn) syrup are

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added to control or prevent crystallization. Chemical differences between carbohydrates similarly can result in different product characteristics. For example, the color of a number of candies is impacted by the choice of sweetener used in manufacturing. Sweeteners also aid in moisture control. Properly chosen, they either prevent moisture loss or moisture uptake. In addition, they add bulk in candies. The following sections discuss the basic chemistry of saccharides and some of their chemical properties. Their physical properties are the subject of Chapter 2.

1.1 Monosaccharides

Saccharides are composed of three basic building blocks, a carbon chain **(–C–C–C)**, hydroxyl groups **(–OH)**, and either an aldehyde **(–CHO)** or ketone **($-CH_2COCH_2-$)** group. The chain length for monosaccharides can vary from three carbons in the simplest sugar to as many as seven. The monosaccharides most important to the confectionery industry are those containing six carbons (glucose, fructose). The presence of either an aldehyde or a ketone group in glucose and fructose gives rise to two categories known as aldose and ketose sugars. The structural difference between the two six-carbon sugars is that glucose contains an aldehyde group while fructose contains a ketone group.

The three most important monosaccharides in candies are glucose, fructose and galatose because their free aldehyde group makes them reducing sugars (defined later) and therefore, they can participate in the browning reactions. In older literature, glucose and fructose are referred to as dextrose and levulose, respectively. These terms arise from the direction in which a plane of polarized light is rotated when passing through a solution of each sugar: glucose rotates a plane of light to the right (dextro) and fructose rotates a plane of light to the left (levulo).

The word dextrose is still used in describing dextrose equivalent (DE), an important property that describes the reducing capacity of starch hydrolysate syrups. The confectionery industry uses the term dextrose when pure glucose is used. The term "glucose" is often used to describe the hydrolysate product of starch, more correctly called starch hydrolysate or glucose syrup.

1.1.1 Glucose/Dextrose

Glucose is widely distributed in nature, including the blood of animals and in the sap of plants. It also forms the base unit in one of the most important polysaccharides, starch, and is an important component of confectionery sweeteners.

Glucose contains asymmetric carbons, those that have four different substitute groups attached, which gives rise to two isomers, designated as D or L glucose. The structure of D-glucose is shown in Figure 1.1. In solution, glucose exists in the pyranose, or ring, configuration in equilibrium with a small amount of the open chain form. By convention, the assignment of the D-form in glucose, or any other monosaccharide, depends on the configuration of the hydroxyl group around the highest-numbered asymmetric carbon. This is most easily seen in the simplest monosaccharide, glyceraldehyde (Figure 1.2). Glyceraldehyde has a three-carbon chain in which only the number two carbon represents an asymmetric carbon. If the hydroxyl group at carbon 2 is written to the right, the structure represents the D-form, whereas if the hydroxyl group is written to the left, the structure represents the L-form. In Figure 1.1, the open chain form (Fisher projection) of glucose has four asymmetric carbons, while the pyranose form has five asymmetric carbons. If the hydroxyl group around the highest-numbered asymmetric carbon, carbon number 5 in glucose, is written to the right, the D form is represented. The isomer of a D-sugar is designated as the L-sugar (Figure 1.3). The open-chain form of glucose has four asymmetric carbons. Since two isomers exist for each asymmetric carbon, in a six-carbon sugar, 4^2 or 16 isomers are possible, eight of which will be in the D-configuration and eight in the L-configuration. The Fisher projections of all D-sugars with chain length between three and six carbons are illustrated in Figure 1.4. Among this family of monosaccharides, glucose, galactose and xylose

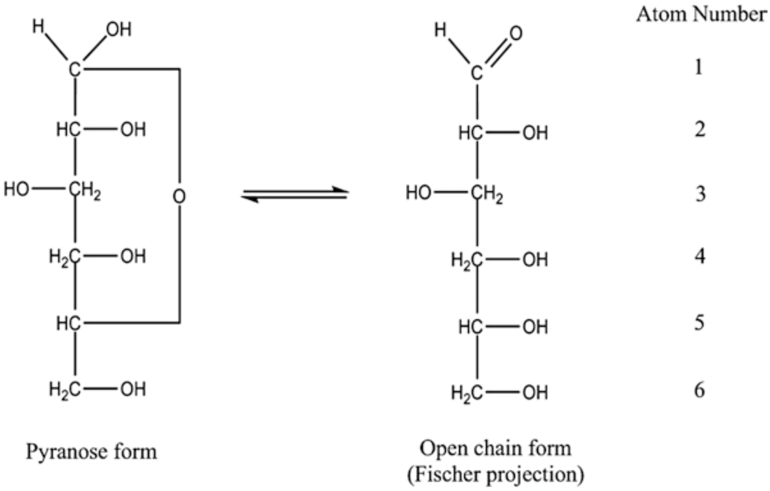

Figure 1.1 Pyranose and open chain forms of D-glucose

are of particular interest to the confectionery industry.

In solution, glucose molecules continuously change from open chain to ring structure and back again. The formation of the pyranose ring introduces an anomeric carbon in the first position (carbon 1), which allows two different orientations of the hydroxyl group as the ring closes. The two possible forms are designated by a Greek letter prefix as α and β. When the carbon 1 hydroxyl group is *cis*- (meaning on the same side) to the hydroxyl group at the carbon 2, the compound is termed α-D-glucopyranose or α-D-glucose. If the two hydroxyl groups are *trans*- (meaning on opposite sides) to one another, the compound is β-D-glucopyranose or β-D-glucose. The structures of α- and β-D-glucose are shown in the pyranose form and in the cyclic Hayworth configuration in Figure 1.5. In the cyclic form, the pyranose ring is considered to be perpendicular to the plane of the paper, with the substituents written to the right below the plane of the ring and those written to the left above the plane of the ring.

Glucose is present in confections primarily through the use of either sucrose or glucose syrups. At times, however, pure glucose/dextrose may be used. Commercial dextrose is made

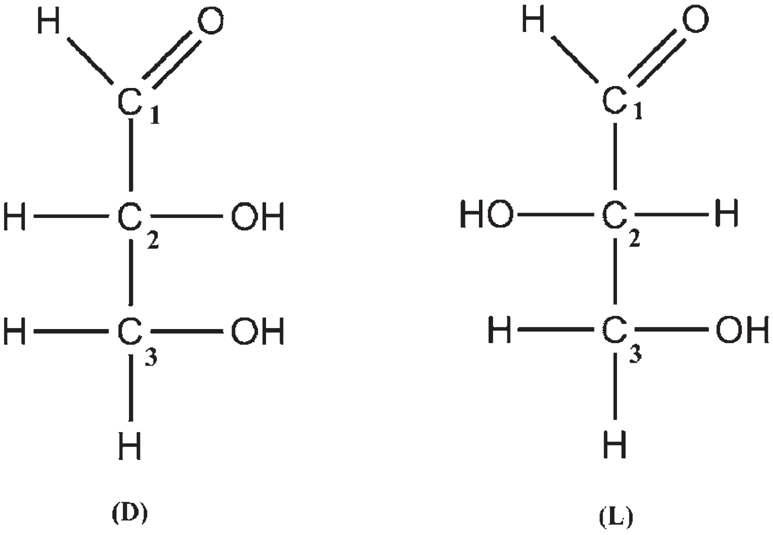

Figure 1.2 Structures of D and L glyceraldehyde

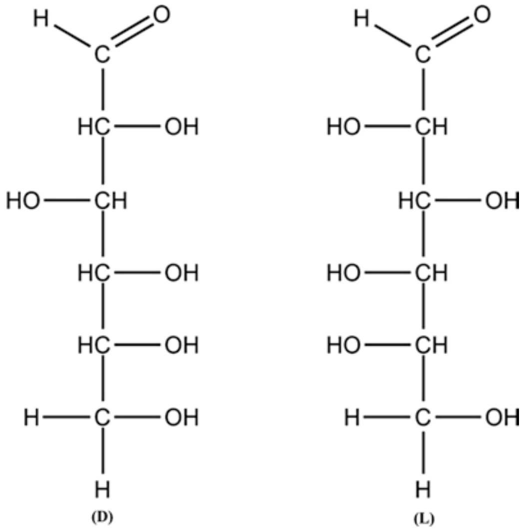

Figure 1.3 D and L isomers of glucose

through purification of fully hydrolyzed starch syrup followed by crystallization and refining. Dextrose crystallizes in different forms, with the monohydrate being the most commonly used. After drying, crystalline dextrose monohydrate is used in a variety of confections. It is often used, for example, directly in pressed tablet confections because of its compression characteristics (see Chapter 7). Anhydrous dextrose is sometimes used in commercial baking chips.

1.1.2 Fructose

The ketose sugar of greatest interest in confections is fructose. Fructose is abundant in nature and occurs in many fruits and vegetables and is a component of honey. Besides honey, it is a component of invert sugar and high fructose glucose (corn) syrup.

The D-forms of fructose in the open-chain, pyranose (six carbon ring), and furanose (five-carbon ring) forms are illustrated in Figure 1.6. These forms coexist in solution, with the pyranose ring form being most prevalent especially at elevated temperatures. As noted above, fructose is also a reducing sugar and, as such, also is found in the α and β isomers.

Until recently, fructose was only available in liquid form; in recent years, processes have been developed for the manufacture of crystalline fructose. However, crystalline fructose is very hygroscopic and care must be exercised in handling to prevent moisture uptake.

The sweetening power of fructose is from 1.3 to 1.7 times greater than sucrose and therefore, it takes less fructose to achieve the same sweetness. Further, since its metabolism does not require insulin, fructose often finds applications in diabetic foods.

1.1.3 Galactose

Galactose is a third monosaccharide of interest in confections. Although it is not used in confections directly, it is of interest because it is one saccharide component of lactose, the milk sugar. The structural comparison of glucose and galactose is shown in the Fischer projection in Figure 1.4.

1.2 Disaccharides

A number of disaccharides are used in confections, although sucrose is far and away the most common. Other disaccharides of interest include maltose and lactose. The chemical structures of these disaccharides are shown in Figure 1.7.

1.2.1 Sucrose

Sucrose is composed of two monosaccharides, α-D-glucose and β-D-fructose, with the glycosidic linkage between the one-carbon of glucose and the two-carbon of fructose. This linkage makes sucrose a nonreducing sugar because it involves the reducing groups of each monosaccharide. Mutarotation is therefore not possible; thus, sucrose cannot participate in the browning reactions unless it is first hydrolyzed (for example, by heat or low pH) into glucose and fructose.

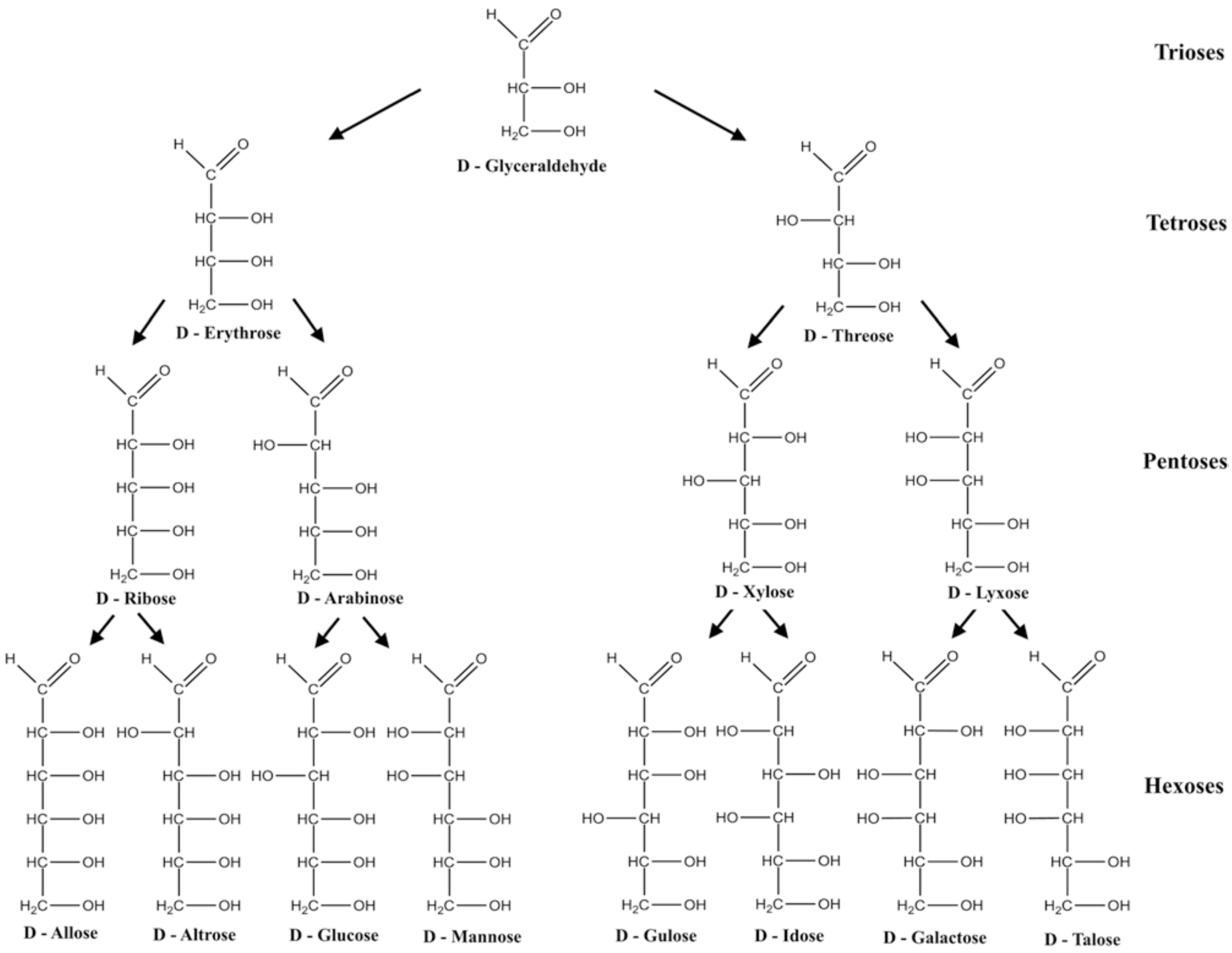

Figure 1.4 Configurational relationship of D-monosaccharides

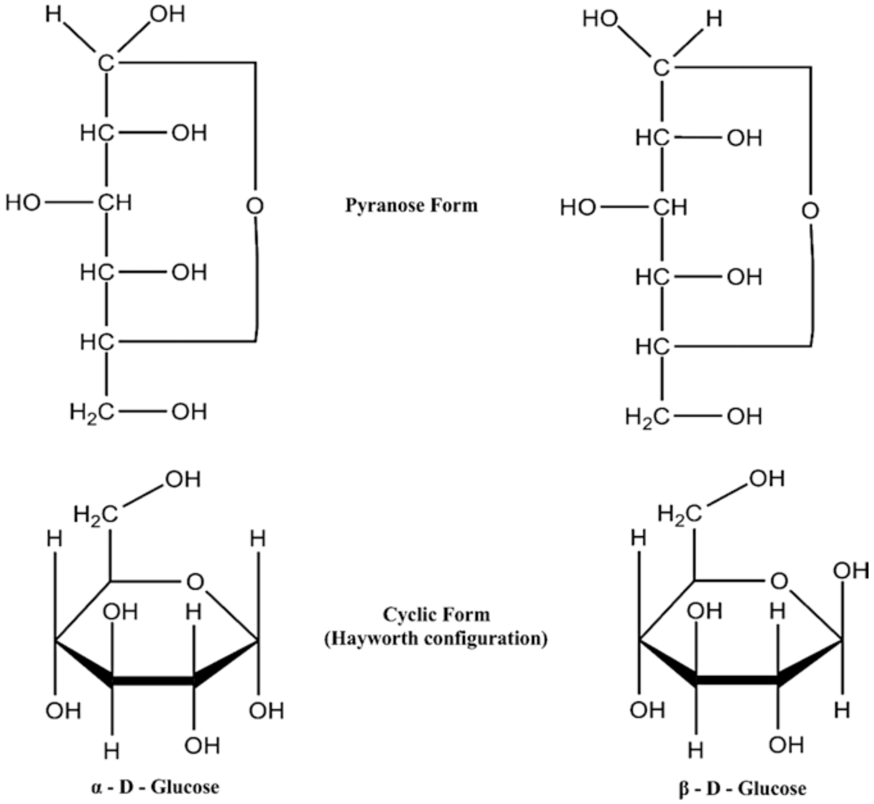

Figure 1.5 Configuration of α- and β-D-glucose

1.2.1.1 Sources of Sucrose

Sugar cane and sugar beets are the two sources of sucrose. Both yield juices rich in sugar that allow, after additional processing, the crystallization of sucrose. In each, the process is complex and a detailed description is beyond the scope of this book. The following summaries give the main steps.

1.2.1.1.1 Cane Sugar

Sugar cane is a tropical grass. It grows up to 7 m tall with stems that reach a diameter of more than 2 cm. At harvest time, the stalks are cut at ground level. Already the next day, sprouts start forming below ground level. Thus, a field of sugar cane, once planted, is self-perpetuating. The pulp in the stalks contains sugar at all times and therefore, there is no real maturity stage. The sugar content increases somewhat with cooler temperatures and decreases with warmer temperatures. Sugar cane typically contains 15% sucrose at optimum maturity, but still contains 12% sucrose several months before and after optimum maturity. This allows for long harvest seasons. However, it is advantageous to harvest cane with the highest possible sugar content.

At the cane processing factory site, the cane is washed to remove as much dirt and debris as possible. One to 2% sugar is lost during this step in the process. Next, the cane is cut into 10–20 cm long sticks, which is followed by a cutting and hammer action to further reduce the cane. The crushed cane is then passed over several mills, which separate the cane into juice and a fibrous residue, called bagasse. Before the last step of milling, the bagasse is washed with water to achieve maximum extraction. Bagasse is waste material, mostly used for fuel.

The juices obtained during crushing and milling are combined and subjected to clarification. At this stage the juice looks brown and muddy. The dissolved materials are sucrose, invert sugar,

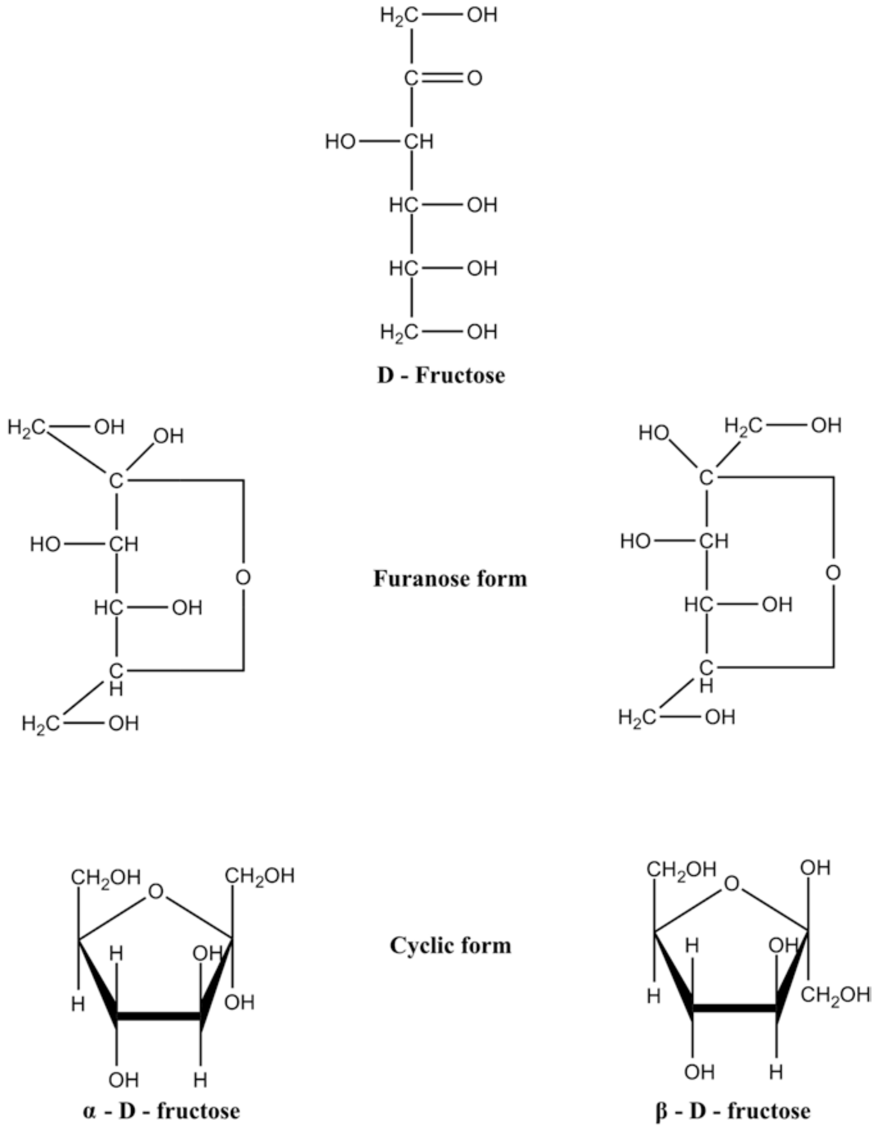

Figure 1.6 Structure of D-fructose and its α and β configurations

salts, silicates, proteins, enzymes, and organic acids. The suspended materials are cane fiber, microorganisms, chlorophyll, gums, starch, waxes, and fat. The first step in clarification is to raise the pH and heat the juice to stop microbial action and to inactivate the enzyme, invertase, which is native to sugarcane. The pH is raised by the addition of lime, which has the added advantage of adding calcium, thus forming and precipitating insoluble calcium salts. Clarification by heat and lime is a process known as “defecation”. The precipitate, or mud, is removed and returned to the field. Following clarification, the juice is called syrup and is dark brown, almost black, in color.

The crystallization and harvesting of sucrose from syrup is accomplished by further evaporation, crystallization and centrifugation. The products of the initial processing steps are raw sugar (crystalline) and molasses. Raw sugar is shipped from the producing areas to the consuming areas, where it is further refined. Refining consists of a

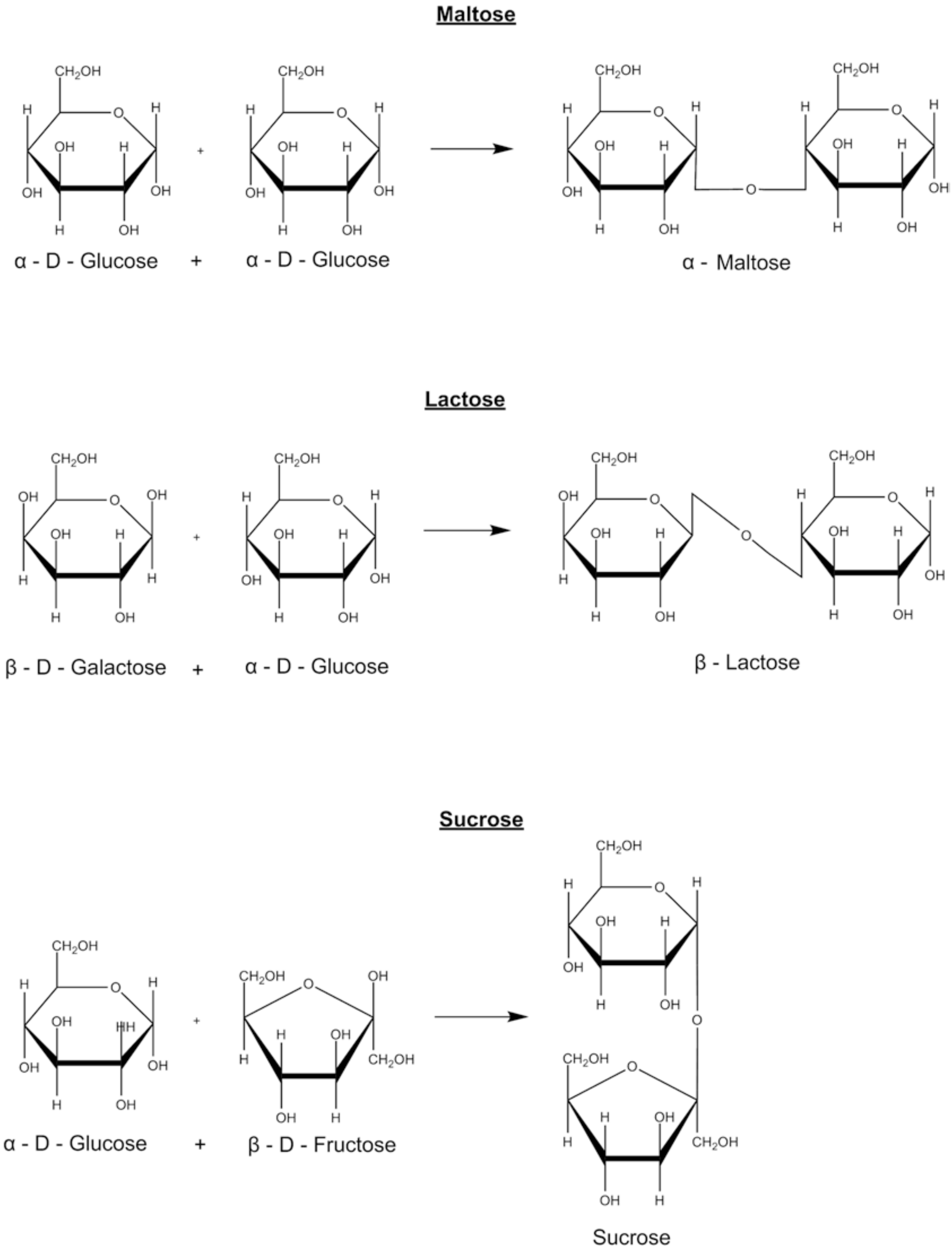

Figure 1.7 Common disaccharides

series of washing and crystallization steps, up to three times, until the final sugar crystals are white with purity greater than 99%. Brown sugar is made by adding some molasses back to the refined sugar crystals.

1.2.1.1.2 Beet Sugar

Sugar beets are grown in northern climates. In the U.S., the largest sugar beet area is the Red River Valley, which lies between Minnesota and North Dakota. This region produces more than 30% of all sugar beets. Sugar beets are seeded in the spring and harvested in October. At harvest time, sugar beets weigh, on average, 1 kg. If not processed immediately after harvest, beets are stored in buildings or in piles as high as 9–10 m (29–32 ft) and as long as 1.5 km (1 mile). Sugar losses during storage are minimal and thus, storage of the beets extends throughout the processing season.

Sugar production begins when beets are removed from the storage facility and enter the factory for a thorough washing to remove soil residues. The cleaned beets are sliced with razor sharp knives into cossettes, which then enter a counter-current diffuser containing hot water. The advantage of cutting cossettes is that it allows for maximum surface area and therefore, maximum sugar extraction. The juice leaves the diffuser for further processing. The cossettes are dried and sold as animal feed. The raw juice from the diffuser is clarified with the addition of lime, similar to the process described for sugarcane, with the impurities removed by filtration. The thin juice is then evaporated to remove excess moisture before it enters a vacuum-pan, where additional water is removed and crystallization is initiated by seeding the syrup with pulverized sugar. Centrifugation separates the white crystals from beet molasses. As for sugar cane, several crystallization and centrifugation steps are used to obtain refined white sucrose.

Beet molasses is not suitable for human consumption and can only be utilized as animal feed or for the production of alcohol. For this reason, brown sugars are not made from beet sugar due to the nature of the molasses.

There has been much discussion as to the merits of the use in confections of cane sugar vs. beet sugar. Today's refined sugars from either cane or beet are practically pure sucrose, 99.9% purity and thus, are virtually indistinguishable. In raw sugars, the differences are greater. Cane sugar has a pleasant flavor and smell, whereas raw beet sugar is bitter and has an unpleasant taste. Less refined beet sugar can have a slight odor and cause excessive foaming. The foaming is the result of incomplete removal of proteins and their breakdown products, saponins and mucilages, neither of which is likely to exist in cane sugar. Less refined cane sugar has been found to contain cane wax, which will act as a foam inhibitor.

1.2.1.2 Sugar Forms and Types

Sugars can be purchased in many forms and crystal sizes. The confectionery industry takes advantage of almost every type of sugar produced. Highly refined sugars are used in chocolate, hard candy, and fondant; brown sugars are used for flavor, for example, in caramel and fudges.

Sucrose may be purchased in many granular sizes. The granular structure of crystallized sugar is determined by the size, shape and the distribution of the crystals. Although the names of the different types of sugar differ between suppliers, they generally fall into five classes, as listed in Table 1.1, based primarily on size. Each of these grades of sugar finds application in the candy industry, although most sugar use is either fine or

Table 1.1 Crystal size and names of sugars

Grain size (μm)	Name of sugar type
	Sanding sugar
>650	Confectioners A
	Confectioners AA
380–635	Coarse
	Granulated
	Fine granulated
175–380	Extra fine
	Granulated
	Baker's special
50–175	Industrial fine
	Crushed fine
<25	Powdered sugar

Table 1.2 Composition of sugars

	Component (%)				
Sugar type	Sucrose	Moisture	Invert	Ash	Others
Sanding	99.98	0.015	0.001	0.002	0.002
Granulated	99.94	0.02	0.015	0.01	0.01
Golden C, (light brown)	89.3	2.7	4.2	1.4	2.4
Yellow D (dark brown)	87.9	2.8	4.6	1.7	3.0

coarse granulated. Larger sizes are used for sanding and decorating while smaller sizes are used when the sugar will not be dissolved and recrystallized, as in pastes and lozenges. Smaller sizes are also used in soft panning to ensure a smooth candy surface.

Table 1.2 gives the composition of some sugar types. For the most part, granulated sugars are highly refined to give greater than 99.9% purity. Brown sugars contain less sucrose and more of the components found in molasses. Powdered sugar generally contains a few percent of starch granules to control moisture and prevent clumping.

Today, a specially manufactured fondant sugar is available to the industry. It is prepared with a fine sugar containing about 3% invert sugar and up to 10% maltodextrin. Fondant sugar allows the manufacturing of a fondant (often called rolled or extruded fondant) without boiling and crystallization procedures (see Chapter 9).

Whether from cane or beet, sugars are most often used in solid form. However, liquid sugar, 67% sucrose dissolved in water (based on the solubility of sucrose in water at room temperature, see Chapter 2), is available and is used in some places in the candy industry. It has the advantage of being pumpable and does not require time for dissolution prior to use. For example, large hard candy manufacturers can pump liquid sugar and glucose syrup together into the evaporator to save both time and energy. While liquid sugars allow for tank storage and economical handing procedures, care must be exercised to avoid microbial spoilage due to the high water activity. Further, crystallization (in containers and even pipes) can occur if temperature is reduced substantially below room temperature and the solution becomes supersaturated (see Chapter 2).

1.2.2 Maltose

Maltose is the combination of two α-D-glucose units. The glycosidic linkage is made between the one carbon of one glucose unit and the four carbon of the second glucose unit. This linkage is referred to as a 1–4 α linkage because the hydroxyl group of the carbon number 1 is in the α position. Maltose is therefore an α-glycoside. It is also a reducing sugar.

Maltose is generally found in confections through addition of glucose syrups (high maltose syrups). It is much less sweet than sucrose (about 0.3 times as sweet).

1.2.3 Lactose

Lactose is the disaccharide found in the milk of mammals. It is the combination of a unit of α-D-glucose and β-D-galactose through the four – carbon of glucose. Lactose, therefore, is a β-glycoside. As a reducing sugar, it participates in the Maillard browning reaction, one of its desired effects in caramel, fudge and toffee.

In confections, lactose is usually introduced through a milk ingredient, as in sweetened condensed milk used for caramel or fudge. Lactose powder is available through refining of whey or whey permeate (after separation of whey proteins). Here, the whey or permeate is evaporated to 60–70% total solids, which supersaturates the lactose. The condensed stream fills a lactose crystallizer, which is then cooled over 18–24 h to produce a crop of lactose monohydrate crystals. These are separated, washed and screened to produce lactose powder. Edible grade lactose is about 97% purity, whereas pharmaceutical-grade lactose is considerably more pure. Crystalline lactose finds its way into many confections, including being used as a nutritive sweetener in chocolate. Its very low sweetening power (0.15–0.25 times that of sucrose) and low solubility (16% at room temperature) are disadvantages in some applications.

1.3 Invert Sugar

Hydrolysis of a sucrose solution yields an equimolar (50/50) mixture of glucose and fructose, a product known as invert sugar, an ingredient that plays an important role in candy manufacturing. In the early days of candy making, before the development of starch hydrolysates, invert sugar was the primary doctoring agent for controlling sucrose crystallization. Often, the presence of invert sugar in confections was, and still is to some extent, due to deliberate processing or ingredient addition that generated a portion of invert sugar in the candy mass. Addition of cream of tartar in production of grained dinner mints, for example, is a holdover of old-time candy making. In principle, a candy maker could now simply add a specified amount of commercial invert sugar and forgo the addition of cream of tartar in making grained mints.

Invert sugar may also be used in confections as a humectant and for flavor release. Due to the low molecular weight of glucose and fructose, invert sugar provides a substantial reduction in water activity (compared to the disaccharide sucrose). This makes it a valuable humectant for products such as fondant and creams. A small amount of invert sugar may also be added to hard candy to enhance flavor release. Also, the combination of glucose (less sweet than sucrose) and fructose (more sweet) ends up being slightly sweeter than sucrose.

Note that invert sugar is formed under normal commercial candy cooking conditions, although the extent of inversion depends on the temperature-time-pH relationship. Slow open kettle boiling to temperatures suitable for hard candy (146–152 °C; 295–305 °F) may create up to 5% (or more if cook time is extended) invert sugar production from sucrose hydrolysis even at neutral pH. In contrast, high throughput vacuum boilers have such a short residence time at elevated temperatures that a negligible amount of inversion occurs.

Commercial invert sugar is produced by either acid or enzyme hydrolysis of a sucrose solution. Most candy companies that use invert sugar in their formulations simply purchase it from a supplier, although some companies still produce their own invert syrups prior to use. However, some of these commercial products are likely to still contain up to 50% unreacted sucrose, which can significantly affect product characteristics.

1.3.1 Acid Hydrolysis

Invert sugar can be produced from sucrose solution with the use of organic acids such as citric, tartaric or acetic acids. With these acids, concentrations of approximately 1% and heating at boiling temperature for 30–45 min are required for inversion, which causes degradation of glucose and fructose and leads to the formation of a dark, generally undesirable, color. A more desirable process for making invert sugar uses hydrochloric acid since it requires a much lower acid concentration (0.1%) and, if allowed to react for 2 h, results in a colorless product. A colorless invert sugar is particularly important in white or pastel colored fondants.

Acid hydrolysis of sucrose is temperature and pH dependent and can be catalyzed by heavy metals. At temperatures above 160 °C, hydrolysis of sucrose will occur regardless of the pH value. It is for this reason that in the manufacturing of hard candy for example, it is important to cool the candy as soon as possible to prevent hydrolysis of sucrose, thereby preventing an increase in the candy's hygroscopic nature that otherwise could cause stickiness. It is for the same reason that in the manufacturing of an acid flavored hard candy, the acid is added during

Table 1.3 The effect of temperature on the hydrolysis of sucrose at pH 2.0

Temperature °C	Time for 99.9% conversion (h)
20	3,511
40	209
80	2

cooling to prevent or minimize hydrolysis and prevent possible stickiness. The influence of temperature of sucrose hydrolysis at pH 2.0is illustrated in Table 1.3.

1.3.2 Enzyme Hydrolysis

The enzyme invertase, typically extracted from cultures of yeast, converts sucrose into invert sugar. There are two enzymes that are capable of hydrolyzing sucrose: β-fructosidase and α-glucosidase. The former acts on the fructose and the latter on the glucose portion of the molecule. The optimum activity for these enzymes is at pH 4–5 and pH 6–7, respectively. Mild temperatures (40–50 °C) are needed for enzyme production of invert syrup since significant losses in enzyme activity occur above 65.6 °C (150 °F), as shown in Table 1.4.

Since the enzyme is also inhibited by soluble solid concentration, enzymatically produced invert syrup should be produced with sucrose concentrations of about 50%. Silver and Karel (1981) document the effects of water activity on the invertase reaction, showing how the reaction rate decreased as water activity decreased (solute concentration increased).

Table 1.4 The effect of temperature on invertase activity

	% loss of activity in	
Temperature °C	20 min	30 min
60.0	4	6
65.6	8	12
71.1	15	20
76.7	20	30

1.4 Sugar Reactions

Although there are other sweeteners used in confections that have not yet been discussed (e.g., glucose syrup), it is important to touch on some of the chemical properties and important reactions of sugars first. Although some of these concepts have been touched on briefly already, this section will provide more details on several important chemical reactions of sugars, including hydrogen bonding, reducing sugars and mutarotation, and browning reactions. Physico-chemical properties, such as sweetness, viscosity, heat of solution, specific optical rotation, refractive index, density, colligative properties, solubility, glass transition, and crystallization, will be covered in more detail in Chapter 2.

1.4.1 Hydrogen Bonding

Water has an enormous ability to hydrogen bond. In a water molecule, the atoms are arranged at an angle of about 105° and the distance between the nuclei of oxygen and hydrogen is 0.957 Å. Each atom carries a slightly positive (hydrogen) or negative (oxygen) charge. Because of the charges, water molecules are attracted to each other with higher than normal van der Waals forces. The

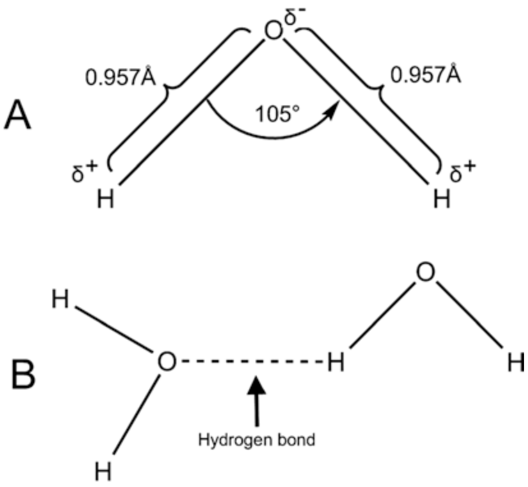

Figure 1.8 (**a**) Structure of a water molecule, (**b**) Attraction of neighboring water molecules through hydrogen bonding

binding energy for a hydrogen bond is approximately 5 kcal per mole. Similar bonding interactions occur, for example, between OH and NH groups. Hydrogen bonding is the reason for the strong affinity of carbohydrates to water.

The structure of a water molecule, and the attraction of neighboring water molecules bonded through hydrogen bonds, is shown in Figure 1.8. The impact of hydrogen bonding can easily be seen by comparing the boiling points of liquids in ascending order of hydrogen bonding capacity. Acetone (CH_3COCH_3) has less hydrogen bonding capacity compared to methanol (CH_3OH) or water (H_2O). The boiling points of these liquids are 53°, 63° and 100 °C, respectively. Thus, it takes far more energy, more hydrogen bonds must be broken, to bring water to its boiling point than to bring methanol to its boiling point.

Water interacts with sweeteners through hydrogen bonding. In fact, a sucrose molecule in solution has on average about five water molecules hydrogen bonded with it (Starzak et al. 2000). But these are not always the same water molecules; since the bonding energy is quite low, there is a continuous interchange of water molecules hydrogen bonding with a sugar molecule. That is, water molecules are continually bonding and releasing from the sugar molecule in an endless interplay. These hydrogen-bonding interactions explain why sugars are so readily dissolved in water.

The nature of the interaction between water and sugar changes as concentration of sugar in solution increases. At higher sugar concentration, sugar molecules begin to interact more with each other and somewhat less with water molecules. This increase in self-association (through hydrogen bonding) continues as concentration increases through and above the solubility concentration, although there is no discontinuity in any chemical property above and below the solubility concentration. In supersaturated solutions, the hydrogen bonding interactions between sugar molecules are thought to form the precursors for the crystalline lattice (Starzak et al. 2000).

Once crystals form in supersaturated solution, hydrogen bonding between sugar molecules becomes predominant. Depending on the sugar, the interactions with water must be released, at least in part, for a crystal to form. In fact, what holds a sugar crystal together is the hydrogen bonding interactions between neighboring molecules in the crystal lattice. Sucrose, for example, forms an anhydrous crystal so that all water molecules must be completely desolvated from a sucrose molecule prior to incorporation of that molecule into the crystal lattice. Other sugars (i.e., glucose, fructose, and lactose) form hydrated crystal lattices, meaning that one (or more) water molecule remains hydrogen bonded to the sugar molecule as that unit incorporates into the crystal lattice.

Hydrogen bonding also influences other interactions of importance in confections. For example, gelatinization of starches is heavily affected by the ability of starch molecules to hydrogen bond. Similar interactions allow hydrocolloids (proteins, gums, etc.) to form the gels needed to provide texture in gummy and jelly candies.

1.4.2 Reducing Sugars and Mutarotation

A reducing sugar is a sugar that contains an aldehyde group or is capable of forming one. In solution, a reducing sugar undergoes mutarotation to form two isomers, α and β. Because a reducing sugar spends a portion of its time in solution in an open form (not a ring form), it is capable of reducing Fehling's solution (Cu^{++} to $Cu^{=}$), as shown in Figure 1.9. The presence of the aldehyde form, an intermediate in the transformation between isomers, allows for the reduction of a cupric ion (Fehling's solution) to a cuprous ion and the formation of gluconic acid. This changes solution color from blue to red.

Mutarotation establishes an equilibrium between the α and β isomers in solution that can be followed by observing the change in optical rotation versus time. For example, if a pure crystalline isomer (say α lactose) is dissolved in solution, the optical rotation (see Chapter 2 for more details) would initially read the value for that isomer. To attain the equilibrium between isomers in solution, some of the α isomer will begin to trans-

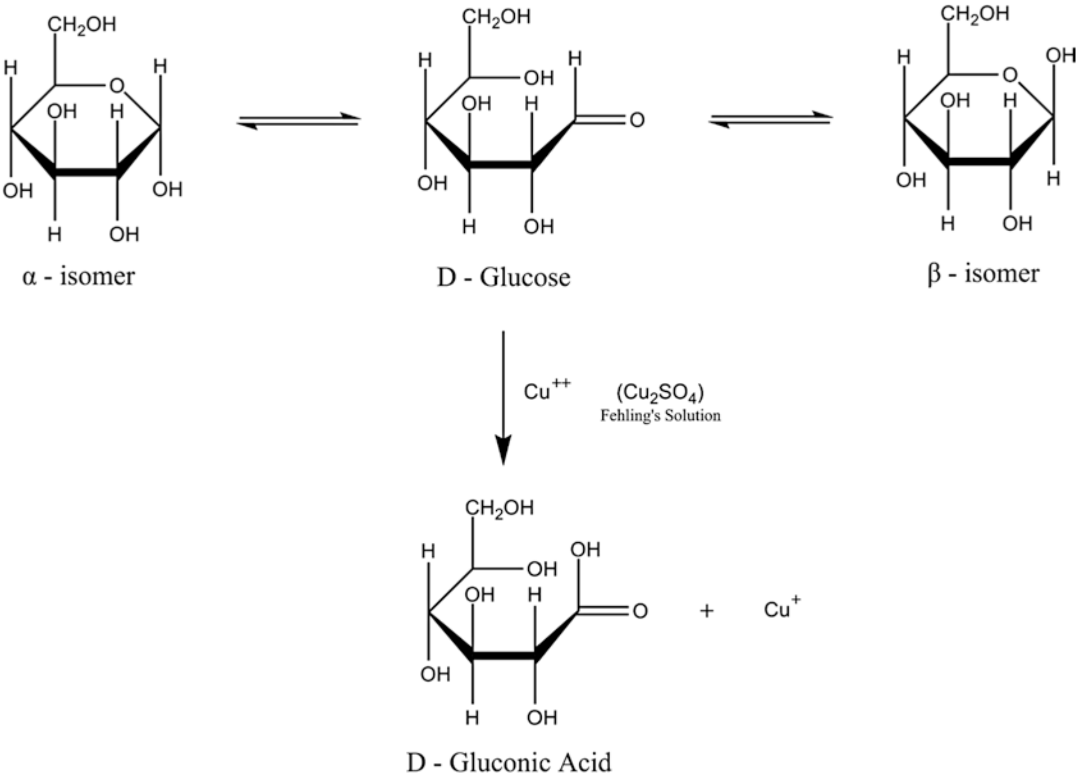

Figure 1.9 Mutarotation of glucose and reduction of cupric ion to cuprous ion

form to the β form, causing a shift in optical rotation dependent on the relative concentrations of the two isomers in solution. Eventually, equilibrium between the two isomers will be reached and the optical rotation of the mixture at equilibrium will be read. Mutarotation equilibrium depends on such solution properties as temperature and pH.

One of the most important properties of reducing sugars is their ability to participate in browning reactions. For one, they can react with proteins in the Maillard browning reaction (often called nonenzymatic browning). Reducing sugars are also needed to initiate the caramelization reaction.

1.4.3 Browning Reactions

In confections such as peanut brittle, caramel, toffee and fudge, the products of caramelization and/or the Maillard reaction are desired for the brown color and some of the flavor. In other products, particularly hard candy, the results of caramelization reactions are undesired since they result in off-color and off-flavor. These reactions are referred to as nonenzymatic browning, in contrast to the often rapid enzymatic (e.g., polyphenol oxidase) browning reaction that occurs in freshly cut vegetables, such as potatoes and apples.

1.4.3.1 Maillard Reaction

Reducing sugars (glucose, fructose, lactose, maltose, etc.) react in the presence of an amine source (typically provided by protein) to form a variety of flavor and color (melanoidins) compounds. The reaction is named after LC Maillard, a French scientist (Billaud and Adrian 2003), who first characterized the reaction. Note that sucrose, as a nonreducing sugar, does not participate by itself in the Maillard reaction. It is only after sucrose has been hydrolyzed (inverted) to form glucose and fructose, both reducing sugars, that Maillard browning can proceed.

The Maillard browning reaction is actually a series of steps that starts with reducing sugars and proteins, develops flavor compounds along the way, and ends with production of high molecular polymers that provide color (van Boekel 2006). Three distinct phases (initial, intermediate, and final, or advanced) are involved, although multiple reactions may take place within each phase:

1. The sugar-amine condensation and Amadori rearrangement,
2. Sugar dehydration and fragmentation, and amino acid degradation by the Strecker reaction, and
3. The formation of heterocyclic nitrogen-containing polymers and copolymers.

To initiate the reaction, the reducing sugars react with the amine to produce a glycosylamine. The amine source can either be an amino acid, a free amino group as part of a protein, or ammonia. This reaction is illustrated in Figure 1.10 with glucose as an example. The next step is referred to as the Amadori rearrangement, which results in the formation of 1-amino-1-deoxy-D-fructose. The reaction continues, even at low pH (<5), to give an intermediate that dehydrates and eventually forms the furan derivative, 5-hydroxymethy-2-furaldehyde (HMF). The reactive cyclic compounds, such as HMF, quickly polymerize into larger compounds called melanoidins, which are both soluble and insoluble, protein-containing polymers (Wang et al. 2011). The melanoidins are primarily responsible for the color arising as a result of the Maillard reaction.

Numerous flavors are generated in the Maillard reaction with the specific compounds formed dependent on the reactants involved and the reaction conditions. Compounds such as pyrazines, pyrroles, pyridines, pyranones, oxazoles, oxalines, furans, and furanones are volatile compounds produced during the Maillard reaction that contribute to flavor. These compounds provide various flavor/aroma characteristics, including caramel-like, cooked, roasted, sweet, burnt, pungent and nutty characteristics (van Boekel 2006). Individual reaction products contribute to overall flavor and aroma with varying intensities. The key to the overall attributes of Maillard browning are determined by the relative concentrations of the individual components produced, which is why the Maillard browning reaction can produce such widely different flavors and aromas.

For example, in chocolate, Maillard reaction products contribute significantly to the desirable flavor and provide the deep rich brown color. The simple sugars present in the cocoa bean react with proteins and peptides, both developed during fermentation. In caramel, fudge, and toffee, the reducing sugars (lactose, glucose syrup polymers, and any sucrose molecules inverted during cooking) react with milk proteins to develop the desired flavor/aroma as well as the desirable brown color.

Differences in Maillard reaction products, and hence color and flavor differences among products, are related to differences in substrate molecules, concentrations, and reaction conditions. Numerous factors have been shown to influence the rate and extent of the Maillard reaction and modify the nature of the compounds produced. Some of these factors are discussed below.

Reactant concentration As with all chemical reactions, the rate of reaction is dependent on reactant concentration, with rate increasing as reactant concentration increases. However, since the Maillard reaction is multi-step, no simple reaction order can be assigned to the entire reaction.

Sugar type The reaction rate is affected by the sugar structure, with reaction rate increasing in the order D-xylose>L-arabinose>hexoses>disaccharides. In general, differences in reaction rate for different sugars are thought to be related to the availability of the open-chain form of the sugar. Sugars that spend more time in the open-chain form undergo Maillard browning more rapidly. Ketoses are less reactive than aldoses, so glucose undergoes the browning reaction faster than fructose. Also, different reaction products

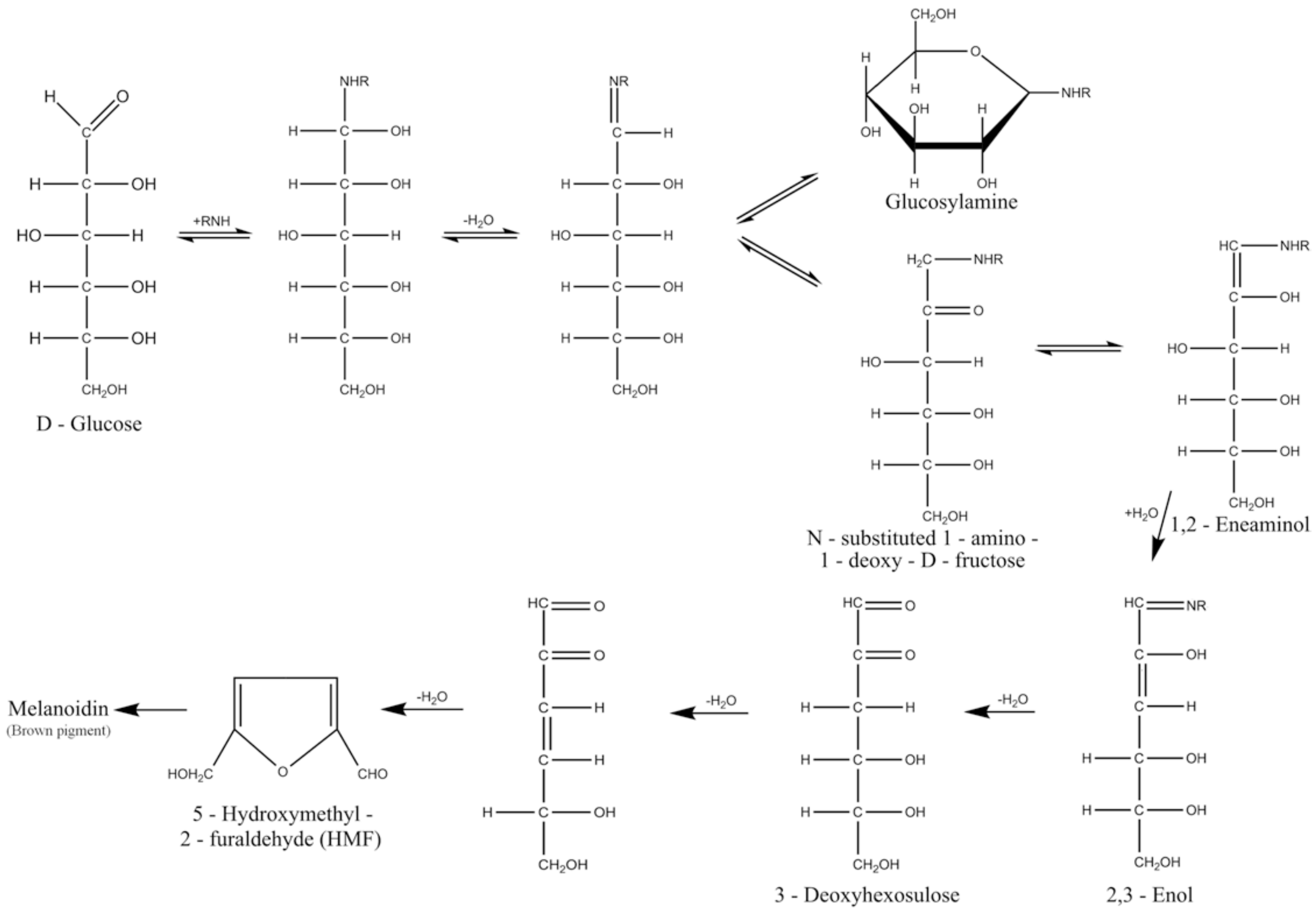

Figure 1.10 Illustration of the Maillard reaction with glucose

are formed with different sugar substrates. In confections, the typical reducing sugars present include glucose and glucose polymers, fructose (hydrolyzed sucrose), and lactose, although they are present at different concentrations and ratios in different confections. This is one of the reasons why the Maillard reaction in caramel (between milk and sugars) gives different flavors from the Maillard reaction on fermented cocoa beans.

Amine source As with the sugar component of the reactants, changing the amino group that participates in the Maillard reaction also influences both the rate of reaction and the nature of the resulting products. Some amino acid groups are more reactive than others, with lysine being a particularly labile group. With proteins, there may be more than one reactive amino group present, further complicating the reaction pathways and products produced.

Temperature As for most chemical reactions, the rate of the reaction increases with increasing temperature, although the effect is complex due to the multi-reaction characteristic of Maillard browning. Each individual reaction that contributes to Maillard browning has its own inherent temperature sensitivity, meaning that the products created vary depending on the temperature of the reaction. Color intensity increases with increasing temperature, as does the carbon content of the melanoidins produced.

pH Both rate and extent of Maillard browning increase with increasing pH over the range of pH 3–9. Due to a change in the reaction pathway as pH changes, the nature of the flavors and color pigments changes as well, although the specific changes are related to the specific reactants. The effects of pH are due to changes in the chemical nature of the reactants, specifically the extent of unprotonated amines and open-chain sugars. In caramel products, buffering salts are sometimes used to control pH, which changes the nature of the browning reaction. Buffers typically increase the rate of Maillard browning although the specific mechanism(s) are still unclear.

Moisture content The rate of Maillard browning exhibits a complex dependence on moisture content due to competing effects. At high moisture content, the reactants are diluted, which decreases reaction rate. As moisture content goes down, the rate goes up, but only to a point. When reactant concentrations are sufficiently high (low moisture content), the viscosity increases dramatically, which ultimately leads to a decrease in molecular mobility and a decrease in the rate of Maillard browning. Thus, there is an optimal water content (about 30%) where browning occurs at the fastest rate.

Minerals and metals Metal ions such as copper and iron act as catalysts and enhance the browning reactions. Fe^{+++} is more effective than Fe^{++}. Also, the mineral components in a confectionery formulation, whether added through hard water and/or milk ingredients, can influence the reaction path by helping to stabilize intermediates and allowing the reaction path to differ. Further, addition of phosphates or carbonates in confections (e.g., caramel) also can influence the reaction path, altering the nature of the flavors, aromas, and color compounds produced.

For more details on the specific nature of the Maillard browning reaction, the reader is referred to van Boekel (2006) and Wang et al. (2011) as well as chapters in food and flavor chemistry books (e.g., Belitz et al. 2004).

1.4.3.2 Caramelization Reaction

Caramelization is the browning reaction that occurs when reducing sugars are heated in the absence of protein (amine groups). In confections, it is an important reaction in production of caramels, particularly in the type of caramel process that first involves browning the sugars prior to cream addition (see Chapter 10). Caramel flavoring (and coloring) is produced in the same way, with sugar being heated in the presence of acid and then base to generate a dark, flavorful mixture that can be added to various products (e.g., licorice, etc.). In hard candy manufacture (Chapter 8), caramelization during cooking of the sugar mass is generally unacceptable since the brown color produced interferes with the normal coloring. Rapid continuous cooking techniques produce essentially colorless cooked sugar syrups by minimizing the time at elevated temperatures to reduce the rate of caramelization.

In the first step of caramelization, reducing sugars undergo dehydration, with glucose being converted into its anhydro sugars, glucosan (1,2-anhydro-a-D-glucose) and levoglucosan (1,6-anhydro-(3-D-glucose). Fructose, when similarly treated, gives rise to lenulosan (2,3-anhydro-p-D-fructofuranose). For sucrose to undergo caramelization, it must first be hydrolyzed into glucose and fructose (which is why acid is added at the start of caramel color/flavor production). Subsequent reactions in caramelization, including fragmentation and polymerization, generally follow the same pathways as seen in the Maillard reaction. In fact, one can think of the two reactions being similar, with the Maillard reaction being catalyzed at lower temperatures by the amine reaction whereas heat (higher temperature) is needed to initiate the sugar dehydration reactions that start caramelization.

Because the general caramelization reaction scheme is similar to that of Maillard browning (after the initial amine reaction), the products of the two reactions are often quite similar, particularly the volatile flavor compounds. Caramelization forms five- and six-membered cyclic ketones such as furanones, cyclohexones and pyrones. The Maillard browning reaction can also form these compounds, but in addition can form nitrogen-containing cyclic structures such as pyrazines, pyrroles and pyridines. Recent studies have begun to provide in-depth characterization of specific odorants found in caramelized sugar samples (Golon and Kuhnert 2012; Paravisini et al. 2012).

The color compounds produced from caramelization are also different from those of Maillard browning due to the lack of protein. In caramelization, color compounds are generally carbohydrate polymers that include caramelan, caramelen, and caramelin, with increasing molecular weight, color and solubility. The specific composition of these brown dyes depends on the type of sugar undergoing the reaction (Golon and Kuhnert 2012).

Due to the similarity of the two reactions, the factors that affect caramelization are generally the same as those that affect Maillard browning, with the exception of the amine group of course.

1.5 Glucose (Corn) Syrup

Glucose syrups created by starch hydrolysis from various plants were first discovered in Russia in 1811, with the presence of dextrose in these syrups confirmed in 1814 (Hull 2010). Discovery of sweet syrups from starch hydrolysis was a fortuitous development due to the sugar shortages during the Napoleonic wars. Interestingly, it was about the same time period when sucrose from sugar beets was first developed, making the history of these two sweeteners, both alternatives to sucrose from sugar cane, follow somewhat parallel paths.

Starch molecules found in plants, such as corn, potato, wheat, rice, tapioca, and the like, are extremely long glucose polymers, either in straight chains (amylose) or branched chains (amylopectin). Glucose syrups, products of starch hydrolysis with sweetness depending on extent of hydrolysis, are produced either by acid, enzyme or a combination of acid and enzyme hydrolysis. According to the standard of identity for sweeteners, the official name is glucose syrup. However, if the syrup is derived from the starch of a specific plant, the name may indicate the source of the starch, which is why in the United States, corn syrup is used almost exclusively. In this book, the term glucose syrup will be used to indicate the increasing trend worldwide.

According to Hull (2010), the industry uses the term "glucose" to indicate a syrup, whereas dextrose is used to indicate the crystalline product (i.e., dextrose monohydrate or anhydrous dextrose).

1.5.1 Glucose Syrup Specifications

In specifying glucose syrups, two properties are of importance: dextrose equivalent (DE) and density, expressed as °Baumé (°Be). Most commercial glucose syrups provide DE and °Be as the primary specifications, with specific saccharide distribution becoming increasingly common as people recognize the importance of knowing the breakdown of individual components. °Be of glucose syrups, as a physical attribute, is covered in more detail in Chapter 2.

1.5.1.1 Dextrose Equivalent

Dextrose equivalent (DE) is a measure of the reducing power of a product, calculated in terms of glucose (dextrose) equivalents and expressed as percent of total dry substance. When starch is hydrolyzed by either acid or enzyme, smaller saccharide fractions (glucose polymers) are formed. Each fraction's terminal unit has a reducing group, regardless of the number of glucose units present in the polymer. In the determination of the DE of syrups, all reducing groups are measured and each is expressed in terms of glucose. Table 1.5 shows a typical glucose syrup composition profile along with the observed DE for each saccharide class. Glucose contributes 100 DE per unit weight, maltose contributes 58 DE, and so on to the longer chain polymers, which contribute less to the overall DE because of their larger molecular weight.

To calculate DE from a saccharide distribution, the relative weight (%) of each saccharide class is multiplied by its observed DE to obtain the contribution of that saccharide class to the total DE. For example, the glucose syrup in Table 1.5 contains 20% dextrose, with a DE of 100. Thus, glucose contributes 20 DE to the total. With 14% maltose in this syrup and an observed DE for maltose of 58.0, the contribution to the total DE is 8.12. Similarly, trisaccharides (maltotriose) contribute 4.74 DE and tetrasaccharides 2.68 DE to the total in accordance with the principle that larger molecules contribute less to dextrose equivalents. Summing the contributions of saccharide class gives the total DE of the syrup. Due to the difficulty in measuring glucose polymers with greater than seven glucose units and their shrinking contribution to DE, the larger molecules are simply lumped into one category for the calculation. The total DE of any glucose syrup can be found in this way, once the saccharide composition has been determined.

It is often necessary to calculate the DE of a glucose syrup blend or a glucose syrup-sucrose blend. In calculating the DE of a mixture, it is important to remember that DE is expressed on a dry weight basis. As an example, calculate the DE of a blend of 60 kg of sucrose with 40 kg of a 36 DE glucose syrup with a solids content of 80.3%. The dry solids (DS) in the mixture are:

$$\begin{gathered}60\text{kg sucrose} = 60 \times 1.00\ \text{DS} = 60\text{kg DS}\\ 40\text{kg glucose syrup} = 40 \times 0.803\ \text{DS} = 32.1\text{kg DS}\\ \text{Total dry solids} = 92.1\text{kg.}\end{gathered}$$

To calculate the % DS of each component, divide the DS of each component by the total DS in the blend:

Table 1.5 Determination of dextrose equivalent (DE) from composition of glucose syrup.

Component	Composition (%)	Observed DE[a]	Contribution to DE
Monosaccharide (glucose)	20	100.0	20.0
Disaccharides (maltose)	14	58.0	8.12
Trisaccharides	12	39.5	4.74
Tetrasaccharides	9	29.8	2.68
Pentasaccharides	8	24.2	1.94
Hexasaccharides	7	20.8	1.46
Heptasaccharides and higher	30	10.2	3.06
Total	100	–	42.0

[a] Equivalent DE of each saccharide

$$\text{Sucrose}\left(60/92.1\right)\times 100 = 61.15\%$$
$$\text{of the total DS is sucrose}$$
$$\text{Glucose Syrup}\left(32.1/92.1\right)\times 100 = 34.84\%$$
$$\text{of totals DS is glucose syrup solids}$$
$$\text{Total solids} = 100.00$$

To calculate the DE of the blend, multiply the DE of each component by its %DE.

$$\text{Sucrose}: 65.1\% \times 0\text{DE} = 0\text{DE}$$
$$36\text{DE glucose syrup}: 34.85\% \times 0.36\text{DE} = 12.55\text{DE}$$

The DE of the blend is 0 + 12.55 = 12.55 DE. Calculations like this are often important in developing formulations that meet quality specifications, as in hard candy for example, where typical DE of the sugar mixture is about 20 DE, to give the desired physical properties.

1.5.2 Production of Glucose Syrups

Production of glucose syrup is accomplished by the hydrolysis of starch (from corn, wheat, etc.) by either acid or enzyme hydrolysis or both.

1.5.2.1 Acid Hydrolysis

The first glucose syrup produced was produced by acid hydrolysis. Acid hydrolysis will hydrolyze starch randomly, cleaving both α-1–4 and α-1–6 linkages between glucose molecules. Under similar conditions of acid, heat and time, the products of starch hydrolysates are the same. Thus, it is possible to produce glucose syrup with the same saccharide composition time after time. Table 1.6 lists the saccharide composition of acid converted corn syrups (43°Be′) in the range of DE 25–55. In theory, it is possible to convert starch by acid hydrolysis to yield only glucose. However, trying to achieve corn syrups with higher than 58–60 DE causes individual mono- and di-saccharides to degrade, forming undesirable colors and flavors that are difficult to remove. Higher DE corn syrups can be produced with additional enzyme hydrolysis.

Table 1.6 Typical saccharide composition of acid converted 43° Baume (Be′) glucose syrup in the range of dextrose equivalent (DE) 25–55

	DE			
Saccharide (%)	25	35	42	55
Glucose	8	13	19	31
Maltose	8	11	14	18
Higher saccharides	84	76	67	51

1.5.2.2 Enzyme Hydrolysis

Enzyme hydrolysis is very specific in contrast to acid hydrolysis, which is random. There are a number of enzymes that have specific action on starch. The actions of the amylase enzymes are shown in Figure 1.11. The enzyme α-amylase (Figure 1.11a) randomly attacks 1-4 glycosidic linkages producing a mixture of saccharides including glucose, maltose, trisaccharides and higher polymer saccharides, or maltodextrins. The formation of maltodextrins occurs because α-amylase is unable to attack 1-6 linkages. The enzyme β-amylase (Figure 1.11b) is more specific. It too attacks α-1–4 linkages, but splits off individual maltose units, thus producing corn syrups with a high maltose content.

There are a series of enzymes that are able to attack either the α-1-4 linkages of amylase or the α-1-6 linkages of amylopectin. Limited dextrinase acts on α-dextrin by attacking α-1–6 linkages, but it requires the presence of some α-1-4 linked glucose residues. It cannot attack amylopectin directly. The R-enzyme can act on amylopectin directly, but it produces only small amounts of simple sugars. Amyloglucosidase has the ability to attack both α and β linkages. Syrups containing a high amount of glucose can be produced by the use of this enzyme.

1.5.3 Composition

The ability to hydrolyze starch by acid, enzymes or a combination of the two allows for the production of various glucose syrups. Glucose syrups produced by both acid and enzyme conversions are referred to as dual converted syrups. In addition, specific blends can be made available to meet manufacturer's specifications.

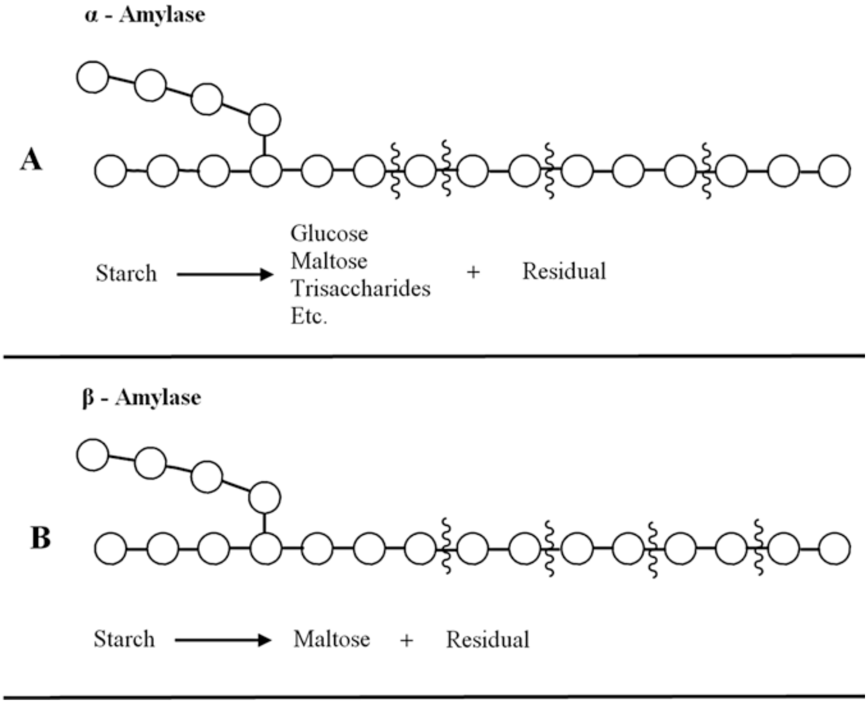

Figure 1.11 Action of amylase enzymes on starch (**a**) α-amylase; (**b**) β-amylase

High maltose syrups can be produced utilizing acid hydrolysis in combination with saccharification by the enzyme, β-amylase. Table 1.7 gives the saccharide composition of several high maltose syrups. The use of other glucoamylase enzymes will result in syrups of different compositions. The application of different types of enzymes has made it possible to produce glucose syrups with DEs higher than 60. The saccharification by amyloglucosidase of an already acid/enzyme converted glucose syrup has produced syrups with DE's ranging between 63 and 95 (Table 1.8). These syrups contain a high percentage of glucose. Typical saccharide compositions of 42 DE glucose syrups hydrolyzed by different methods are shown in Table 1.9. Glucose syrups are often referred to by the degree of conversion – low, regular, intermediate, high and extra high. The range in DE for each is given in Table 1.10.

Because of the unique saccharide distribution, each glucose syrup has a different average molecular weight, depending on degree and nature of the hydrolysis. Technically, calculation of average molecular weight is done by first calculating the mole fraction of each saccharide and the summing the mole fractions times molecular weight of each saccharide. Pancoast and Junk (1980) provide average molecular weight values for certain types of glucose syrups. For example, they

Table 1.7 Typical saccharide composition of high maltose syrups with different dextrose equivalent (DE) converted by acid/enzyme

	DE		
Saccharide (%)	36	42	50
Glucose	6	8	10
Maltose	35	40	50
Higher saccharides	59	52	49

Table 1.8 Typical saccharide composition of high dextrose equivalent (DE) glucose syrups converted by either acid/enzymes or enzyme/enzyme

	DE		
Saccharide (%)	63	70	95
Glucose	38	45	94
Maltose	34	31	3
Higher saccharides	28	24	3

Table 1.9 Typical saccharide composition of 42 dextrose equivalent (DE) glucose syrups converted by three different methods

Saccharide (%)	Type of conversion		
	Acid	Acid/enzyme	Enzyme
Glucose	19	6	2
Maltose	34	45	55
Trisaccharides	12	12	18
Higher saccharides	55	35	25

quote 36 and 42 DE acid-converted syrups to have average molecular weights of 543 and 430, respectively, while a 62 DE acid-enzyme converted glucose syrup has an average molecular weight of 296. As expected, average molecular weight decreases as DE increases since more lower molecular weight fragments are produced with higher degree of hydrolysis. Although average molecular weight is what influences properties such as boiling point elevation, it is rare that candy makers use this level of detail.

The final end product of starch hydrolysis is the production of glucose (dextrose), when each polymer unit is completely hydrolyzed. It can be further refined, and sold as crystalline dextrose monohydrate, which contains one molecule of water for every molecule of glucose, or anhydrous dextrose. Dextrose is also sold as a liquid, but it has the disadvantage that it must be stored between 49 and 52 °C to prevent crystallization.

In the late 1960s, a process was developed to isomerize glucose to fructose in starch hydrolysates. The process is an enzyme reaction with glucose isomerase in an immobilized enzyme reactor. The product is known as high fructose (corn) syrup (HFCS). The first HFCS available was a syrup containing 71% solids composed of 42% fructose, 52% glucose, and 6% other saccharides. Because of the high glucose concentration, storage temperatures between 27 and 32 °C are required to prevent glucose crystallization. In 1976, a 55% HFCS was developed. The process involves a fructose enrichment step, since isomerization of glucose to fructose by enzymes above 42% is not possible. Typically, 55% HFCS contains 77% solids composed of 55% fructose, 42% glucose, and 4% other saccharides. This syrup can be used to replace invert sugar. Its other advantage, because of its lower glucose content, is that it can be stored at lower temperatures, from 24 to 29 °C. Today, a 90% HFCS product is available. This syrup has a typical solid content of 80% and contains 90% fructose, 7% glucose, and 3% other saccharides. It can be stored at lower temperature, but 21–26 °C is recommended, mainly to facilitate handling of materials containing 80% solids.

Table 1.10 Common nomenclature of glucose syrups by dextrose equivalent (DE)

Corn syrup	DE range
Low conversion	26–37
Regular conversion	38–47
Intermediate conversion	48–57
High conversion	58–67
Extra high conversion	68 and higher

1.5.4 Properties

Glucose syrups are major ingredients in confections. In addition to the food value they provide, glucose syrups are used to control sweetness, texture, crystallization, browning, and humectancy. Because of the greater solubility of glucose syrups compared to sucrose, a mixture of sucrose and glucose syrup has a greater concentration than sucrose alone, with soluble solid concentrations of 75% and higher easily reached. The relationship of functional uses or properties of glucose syrups as affected by the degree of conversion is illustrated in Figure 1.12. As the DE increases, the degree of hydrolysis increases, the syrup contains more glucose and maltose, and becomes sweeter. In practice, sweetness is also affected by temperature, pH, and other substances. Table 1.11 compares the sweetness of a number of glucose syrups against sucrose.

Lower DE glucose syrups, because of their greater percentage of long-chain residuals, increase the texture or body strength and are said to increase the ability to prevent crystallization. In the latter case, the long chain residuals are thought to prevent sucrose molecules from associating to form a crystal.

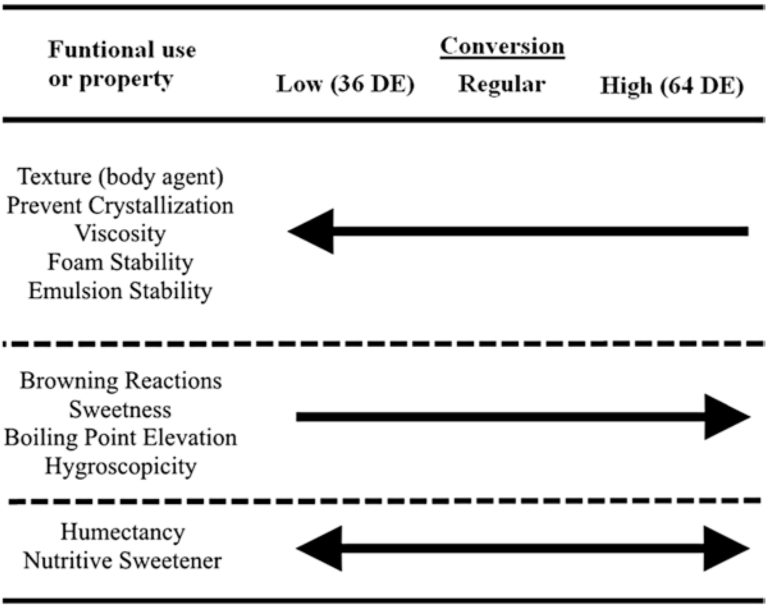

Figure 1.12 Relation of functional use or property of glucose syrup to the degree of conversion

High DE glucose syrups have greater numbers of reducing groups and therefore, products of the caramelization and/or Maillard reaction increase. Similarly, as the DE of a glucose syrup increases, it becomes more hygroscopic, and confections containing high levels of high- conversion syrups must be physically protected to minimize water up-take. Products containing low DE syrups are less hygroscopic and are therefore less likely to absorb water. They will also retain their moisture for longer periods of time. The use of glucose syrups to control humectancy will depend on the characteristics of the product.

Two other properties of glucose syrups that are affected by the DE are the boiling point and viscosity. As the DE of glucose syrup increases, the boiling point increases and the viscosity decreases. The elevation of the boiling point of a solution is dependent on the number of molecules in solution. A solution containing a high DE glucose syrup will have higher boiling point than a solution containing low conversion glucose syrup.

Table 1.11 Sweetness of glucose syrups of different dextrose equivalent (DE) compared to sucrose

Glucose syrup	Relative sweetness
30 DE acid –converted	30–35
36 DE acid – converted	35–40
42 DE acid – converted	45–50
62 DE acid – converted	60–70
HFCS[a] 42% fructose	100
HFCS 55% fructose	100–110
HFCS 90% fructose	120–160

[a]High fructose corn syrup

With the reduction of high molecular weight fractions, or polysaccharides, in high conversion glucose syrups, the viscosity is reduced. Therefore, a 36 DE glucose syrup has significantly higher viscosity than a 62 DE glucose syrup at the same temperature and solids concentration.

More details on the physical properties of glucose syrups are provided in Chapter 2.

1.6 Polysaccharides

Polysaccharides are used in candies primarily as bulking agents. There are three major types: maltodextrin, polydextrose, and inulin.

1.6.1 Maltodextrin

Maltodextrin is a dried starch hydrolysate with a low DE, from as low as 1 and up to a maximum of 20 (above 20, it is technically called glucose syrup). Depending on DE, maltodextrins contain predominantly longer-chain, higher molecular weight saccharides between 3 and 17 glucose units (degree of polymerization, or DP, from 3 to 17). A 10 DE maltodextrin, for example, contains on the order of 64% saccharides above DP 11.

Functionally, maltodextrin is not hygroscopic and dries into a noncrystalline (amorphous) powder. Because of its low sweetness, it must be used in combination with other alternative sweeteners. In confections, besides acting as a bulking agent, maltodextrins may be used to provide foam stabilization (due to high viscosity), control sucrose crystallization, form barrier layers prior to sugar panning, act as a glaze on panned goods, and serve as a binder in tabletted confections.

1.6.2 Polydextrose

Polydextrose is a randomly-bonded polymer of glucose with minor quantities of sorbitol and citric acid incorporated into the polymeric chain. It is prepared by vacuum condensation of a molten mixture of glucose, sorbitol, and citric acid at a ratio of 89:10:1. The polymer size is controlled by the presence of the sorbitol, with most polymers having molecular weight less than 5,000 g/mole. For this reason, polydextrose is very water soluble. However, solutions containing more than 70% solids become impractical to work with because of the high viscosity. Polydextrose is a white to light tan powder with a bland to slight bitter taste. Several different forms are available on the market depending on the application.

Human enzymes do not recognize most complex polymers because of their random nature. Therefore, polydextrose contains only 1 kcal/g and is considered a soluble fiber. It has no sweetness, but possesses most of the other chemical and physical properties of sucrose, making it a good sugar replacer.

1.6.3 Inulin

Inulin, another soluble fiber, is a natural occurring polysaccharide – a polymer of fructose (Izzo 2002). It is found naturally in onion, leek, chicory, and Jerusalem artichoke, among other plants. It is a β (2–1) fructan with chain length ranging from 2 to more than 60 fructose units (average of about 10 units), with a glucose molecule typically at the polymer terminus. Manufacturing processes involve similar steps as used for refining sucrose – water extraction from the plant source, purification followed by spray drying. It has a slightly sweet taste and low water solubility. It has low reducing power, but is subject to acid hydrolysis, yielding fructose. As with polydextrose, it is not digested and thus, has reduced caloric value of approximately 2 kcal/g.

Inulin contributes to texture in confections. It can be used to replace sugar and provide a source of fiber in fruit chews, caramels, high fiber lozenges, and chocolates and coatings (Izzo 2002).

1.7 Other Natural Sweeteners

Honey, maple syrup, molasses, and malt extract are also sweeteners in confections. Although they have sweetening properties, they are mostly used as flavor ingredients.

1.7.1 Honey

Honey, no doubt, is the oldest and original sweetener. Its use long preceded the development of sugar. In essence, honey is a natural high invert

Table 1.12 Composition (%) of United States honey

Composition	Average	Range
Moisture	17.2 ± 1.5	13.4–22.9
Fructose	38.2 ± 2.1	27.2–44.3
Glucose	31.3 ± 3.0	22.0–40.7
Free acid (as Gluconic)	0.43 ± 0.16	0.13–0.92
Lactone	0.14 ± 0.07	0.00–0.37
Ash	0.169 ± 0.15	0.020–1.028

sugar, containing primarily glucose and fructose. The composition of honey can vary considerably, depending on a variety of factors. Table 1.12 lists the average composition of U.S. honey. The fructose content is always higher than the glucose content with the ratio varying between 1.15 and 1.35.

Honey is used essentially for flavor purposes in confectionery, although it also retards sucrose crystallization. The flavor depends on the source of nectar. Clover and orange blossom honey have a very delicate flavor and are preferred. Alfalfa and buckwheat honey have very strong flavors. Honey varies in color from amber to white.

1.7.2 Maple Syrup

Maple syrup is produced in northeastern and midwestern United States and Canada. It is prepared by evaporating the sap from the maple tree. Sap contains between 2 and 3 wt% solids of which approximately 96% is sucrose and the remainder other carbohydrates, protein, organic acids, ash, and lignin-like materials. Maple syrup, by federal specification, must contain 66 wt% solids with a specific gravity of 1.35 (37.75 Be′). Flavor and color develop during the evaporation process as a result of both the caramelization and Maillard reactions (see Section 4.3).

Typical saccharide composition of maple syrup is 88–99 wt% sucrose and 0–12 wt% invert sugar. Crystallized maple syrup candies must be made with minimal invert sugar content to attain the desired crystallinity and texture.

In confections, maple syrup is primarily used for its unique flavor. Because of price considerations, artificial maple flavor is often substituted; however, real maple syrup still finds application in fudges and creams, particularly in combination with walnuts.

1.7.3 Molasses

Edible molasses as described earlier is the by-product of cane sugar refining. In the refining process, several sugar crystallization steps take place to further purify the sucrose for separation. After the first crystallization, the mother liquid is called first molasses. First molasses is recrystallized, resulting in additional sucrose separation and a second molasses. After a third crystallization, the third molasses is sold as blackstrap, final or can molasses. The raw sugar obtained from these crystallizations is combined with water to dissolve residual molasses and is separated by centrifuge. The separated syrup is called affination liquor. The sugar is dissolved in water and subjected to several crystallizations. The mother liquid from the final crystallization is combined with the affination liquor and crystallized to produce a dark sugar and a mother liquid refiners molasses. It is similar to final molasses, but of better quality.

Typical molasses contains 80 wt% solid with 60 wt% as invert sugar. It also contains numerous vitamins and minerals. Because of this large amount of invert sugar, molasses inhibits sucrose crystallization. Molasses can be dried and is available in powdered form.

Molasses is commonly used as a flavorant in licorice, but also may be used in such confections as taffy, hard candy, creams, and caramel to provide unique flavoring. One unique candy made with molasses (and peanut butter) is the Mary Jane, a chewy (taffy-like) old-time candy.

1.7.4 Malt Extract

Malt extract, available as either a concentrated extract or a powder, is manufactured from high grade brewing barley. It is considered a sweetening ingredient because of its high maltose content. To make malt extract, barley kernels are wetted and allowed to germinate under controlled conditions of temperature and humidity. During germination, the starch is solubilized by enzyme action and the protein is partially degraded to peptides and amino acids. This step is followed by kiln drying in which the enzymes are retained. The germinated and dried grain is then extracted with water, and the extract filtered and concentrated to 80% total solids. The concentrate may be vacuum dried to produce a powder. The saccharide composition of an extract of 80% solids is approximately 55% maltose, 4% sucrose, 2% glucose, 2% fructose and 13% dextrins. Such a syrup resembles a high-maltose syrup but also contains some protein as well as amino acids, vitamins and minerals.

Malt extract has specific application in confections as a flavoring ingredient. Arguably the most popular candy containing malt extract is the malted milk ball, a puffed sugar candy coated with chocolate.

1.8 Alternative Sweeteners

Sucrose has been and remains a main ingredient in confections. Its desirable physical and chemical properties have made possible the development of many different confections; it has made confections popular throughout the world. In addition, sucrose is an excellent source of energy, at relative low cost.

Over the past few decades, however, sucrose has been a subject of controversy over its nutritional role in the diet. Studies and debates have centered around the involvement of sucrose in such issues as dental caries, obesity, diabetes, hypertension, hypoglycemia, and behavioral problems. Each of these issues have influenced the consuming public's attitude toward sucrose and has created a demand for no-sucrose or "sugar-less" confections to avoid the negative nutritional aspects of sugar, whether real or perceived. The challenge, therefore, has been to find sugar alternatives that both retain most of the beneficial properties of sucrose yet eliminate, or at least minimize, the concerns of the consumer. The most used sucrose alternatives are sugar alcohols, hydrogenated starch hydrolysates (HSH), polydextrose, and intense sweeteners.

1.8.1 Sugar Alcohols

Sugar alcohols, also known as polyols, are not sugars, but are the reduced form of sugars. They occur in nature, but at low concentrations, which make extraction impractical. They are industrially derived from the corresponding saccharide by catalytic hydrogenation, with the exception of erythritol, which is prepared by fermentation of glucose. The general reaction to form the alcohol from a sugar is shown in Figure 1.13 for hydrogenation of glucose into sorbitol. In the reaction, a hydroxyl group replaces either the ketone or aldehyde group of the sugar. Hydrogenation of fructose yields mannitol, xylose yields xylitol, maltose yields maltitol, lactose yields lactitol, and finally, hydrogenation of glucose syrup yields hydrogenated starch hydrolysates (HSH).

Polyols play an important role in confectionery products, particularly those targeted towards the diabetic market because of their lack of an insulin response. They are also used to provide caloric reduction due to their limited absorption in the stomach despite the laxative effect due to their subsequent fermentation in the intestines. Polyols can also provide humectancy, reduction of water activity and control of crystallization in confections. Most polyols provide a significant cooling effect and are noncariogenic. Because they are nonreducing, they also do not participate in either browning reaction. A summary of various properties of polyols is provided in Table 1.13.

1.8.1.1 General Properties of polyols

Polyols do not exhibit reducing power, because the aldehyde group of the sugar has been reduced to an alcohol. They therefore do not undergo the caramelization or the Maillard reactions. Thus, if the typical brown color generated in these reactions is desirable in a confection, as in caramel, fudge or toffee, artificial colors must be added to a sugar-free version based on polyols. Polyols are also mostly stable to acids and can withstand high temperatures for extended time. If discoloration does occur in polyol solutions, hydrolysis must first take place. For example, maltitol hydrolysis yields glucose and sorbitol, and the glucose molecule can now participate in either or both browning reactions.

Polyols, with the exception of xylitol, are less sweet than sucrose (Table 1.13). In many confectionery applications, the lower sweetness of polyols is offset with the addition of intense

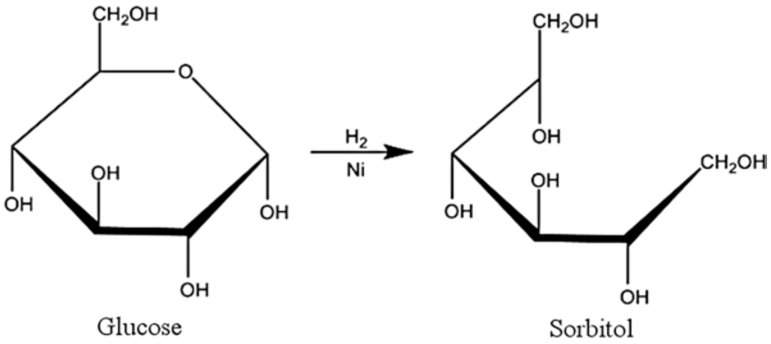

Figure 1.13 Catalytic hydrogenation of glucose

sweeteners, but this depends to a large extent on which polyols are used in a formulation.

Polyols have a higher negative heat of solution compared to sucrose, with the exception of maltitol, which has a negative heat of solution similar to sucrose (Table 1.13). When the crystalline forms dissolve in water a cooling effect is observed. This pleasant cooling sensation can be an advantage in enhancing consumer enjoyment in such products as mint-flavored candies. More details are provided on heats of dilution and solution in Chapter 2.

Polyols are virtually nonfermentable and are, therefore, considered noncariogenic. The nonfermentable characteristic by oral bacteria prevents acid production and reduction in pH value, conditions that are associated with tooth decay. In the intestine, they are slowly absorbed and enter the liver without the need for insulin. They are converted to fructose and ingestion of polyols therefore results in lower plasma glucose. For this reason, polyols are recommended for diabetics. Products that are sold for use by diabetics are required by the United States Food and Drug Administration (FDA) to carry the labeling statement "Diabetics: This product may be useful in your diet on the advise of a physician." However, the incomplete digestion and slow absorption of polyols can lead to gastrointestinal problems. This can occur if excessive amounts are consumed at one time, but in some people, there can also be a cumulative effect. The extent of the laxative effect depends on the polyol consumed. A daily threshold value for each polyols is given in Table 1.13. FDA requires that if it is reasonably foreseeable that consumption may exceed the threshold value, the label statement, "excessive consumption may have a laxative effect" must be given.

The slow absorption rates of polyols are responsible for their lower caloric content compared to sugar. Caloric content (in kcal/g) for different polyols are listed in Table 1.13. The values listed are those for the United States. Other coun-

Table 1.13 Properties of polyols

Polyol	Relative sweetness	Laxation threshold (g/day)	Solubility 25 °C (g/100ml)	Heat of solution (cal/g)	Caloric content (kcal/g)
Erythritol	60–70	High	61	−43.9	0
Xylitol	100	50	200	36.6	2.4
Sorbitol	60	50	235	−26.5	2.6
Mannitol	50	20	22	−28.9	1.6
Maltitol	90	100	175	−5.5	3.0
Lactitol	40	20–50	140	−13.9	2.0
Isomalt	40–50	50	39	−9.4	2.0
Sucrose	100	–	185	−4.5	4.0

tries may use slightly different values. In fact, Europe simply states that caloric content of all polyols is 2.4 kcal/g, regardless.

One final property of note for polyols is viscosity. As with all sugars, viscosity of polyol syrups increases with increasing concentration in solution and with decreasing temperature. However, the viscosity of a saturated solution of polyols follows a different trend from that of sucrose and this can have significant ramifications where solution viscosity is important, as in hard panning (see Chapter 13). Unlike for sugars, where viscosity at saturation decreases with increasing temperature, the viscosity of some saturated polyol solutions increases with increasing temperature, dependent on the relative effects of temperature on solubility and viscosity. See Chapter 2 for more on sweetener viscosity.

1.8.2 Monosaccharide Alcohols

The monosaccharide sugar alcohols comprise a major category of polyols used in confections. Of particular interest are sorbitol, mannitol, xylitol, and, to some extent, erythritol.

1.8.2.1 Sorbitol

Sorbitol is the most widely distributed natural polyol. It is found in many fruits such as cherries, plums, apples and pears. It is commercially produced by catalytic conversion of D-glucose (Figure 1.13). It was first isolated from a mountain berry called "sorb apple", from which it derived its name. It is available in ether crystalline or liquid form at concentration of 70%. The liquid form may contain small amounts of mannitol to prevent crystallization. It is most often found in sugar-free gum, but may also be used in pressed tablets and hard candy. Its high hygroscopic nature makes it an excellent humectant. In chewing gum, for example, sorbitol retards the loss of moisture and prevents drying out of the gum. Sorbitol can also be used for hard panning although it is not widely used for that purpose.

Crystalline sorbitol is polymorphic, meaning that it can exist in multiple crystalline forms. The γ polymorph is the most stable, with a melting point of about 98–99 °C (Nezzal et al. 2009). The α and β forms are very hygroscopic and therefore, have limited application. Under the influence of moisture and heat, the unstable forms transform to the stable, γ, form.

1.8.2.2 Mannitol

Mannitol is found in nature in algae, mushrooms, celery and olives. Originally, it was commercially extracted from algae, but today it is produced by hydrogenation of fructose. The hydrogenation of fructose yields both mannitol and sorbitol. The reaction is shown in Figure 1.14, as illustrated in the Fischer projection to clearly show that hydrogenation creates an asymmetric carbon at carbon 2 and thus, results in two isomers, sorbitol and mannitol. Because of the mixture of polyols during hydrogenation, the manufacturing process must include a separation step, which makes the manufacturing of mannitol a more expensive process. Pure mannitol, because of its low solubility (Table 1.13), can be crystallized and is available only as a powder. Its low hygroscopicity and excellent flow characteristics make mannitol a valuable ingredient in tableted confections. It may also be used in sugar-free chocolate and as a dusting powder in chewing gum.

1.8.2.3 Xylitol

Xylose is found in nature in woody plants and a number of fruits and vegetables. Xylitol was first produced by hydrolyzing xylan from birch trees to form xylose and then hydrogenating xylose to form xylitol. It is a pentahydric alcohol, which means it has a five-carbon chain, in contrast to sorbitol and mannitol, which are polyhydric alcohols and have six-carbon chains. Today, any hemicelluose source, such as corn cobs, may be used as raw material. It is commercially available as a white crystalline powder.

Xylitol is hygroscopic, with moisture uptake accelerating rapidly at relative humidity above 80%. It is less hygroscopic compared to sorbitol, which begins to absorb moisture above 70% relative humidity. Xylitol solutions are heat stable, withstanding temperatures as high as 200 °C. The viscosity of xylitol is lower than sucrose or other polyols. The low viscosity may affect the texture

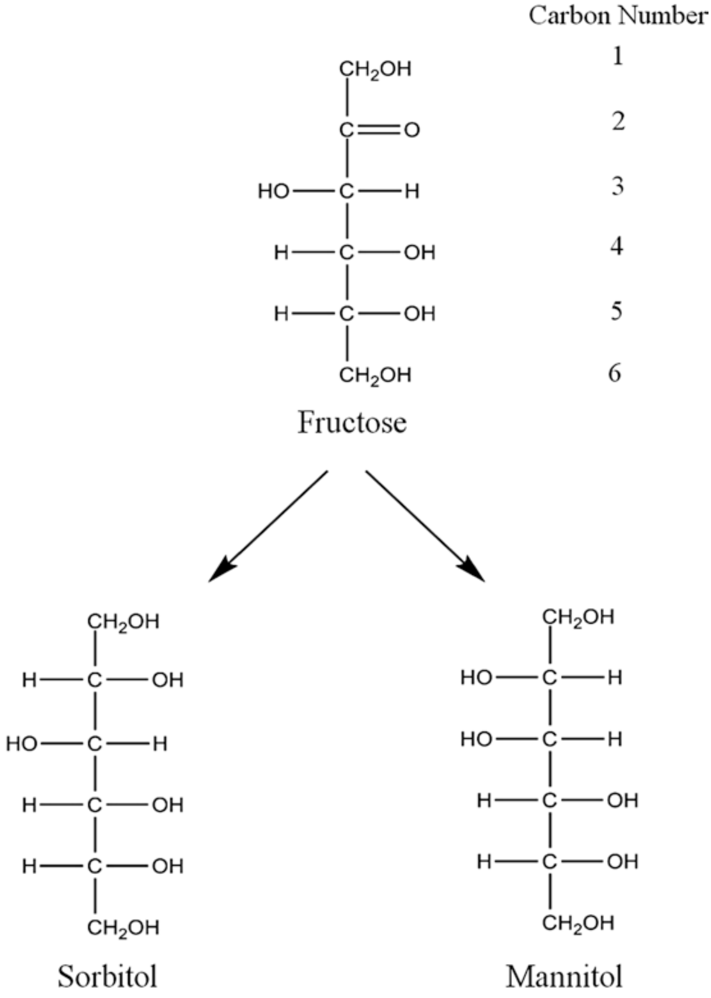

Figure 1.14 Catalytic hydrogenation of fructose

of confections and the addition of a bodying agent such as polydextrose may be required. Because of its high cost of production, and its sweetness level similar to sucrose, it is often mixed with other, less expensive sweeteners. Xylitol is recognized as the most effective among all polyols in preventing caries. There is evidence to suggest that xylitol may even be anticariogenic.

In confections, xylitol is most often used in sugar-free gums, both within the gum as well as in a hard-panned shell. Its relatively rapid crystallization rate makes it useful in hard-panned shells. It may also be used in pressed tablets. Its high cost often limits its use.

1.8.2.4 Erythritol

Erythritol is the only 4-carbon chain polyol. It is the reduced form of erythrose (Figure 1.4). Erythritol is produced by yeast fermentation of glucose, meaning it can potentially be used in natural products. In human metabolism, it is absorbed and excreted unchanged via the kidney, which explains its low caloric content (Table 1.13). It has the highest negative heat of solution among all polyols, which is its major functional limitation. While the extreme cooling sensation when eaten goes well with mint pieces, it is not generally a desired effect.

1.8.3 Disaccharide Alcohols

Disaccharide alcohols have become important confectionery ingredients. These include isomalt, maltitol, and lactitol.

1.8.3.1 Isomalt

Isomalt is produced from sucrose in a unique two-step process. Sucrose, a nonreducing sugar, is first transformed by the enzyme sucrose-glucosylfructose-mutase into a reducing sugar, isomaltulose. In this transformation the 1-2 linkage is converted to a 1-6 linkage, thus forming a free ketone group at the fructose molecule. Isomaltulose is than hydrogenated to give isomalt, an equimolar mixture of gluco-sorbitol (α-D-glucopyranosyl- (1-6)-D-sorbitol) and gluco-mannitol (α-D-glucopyranosyl-

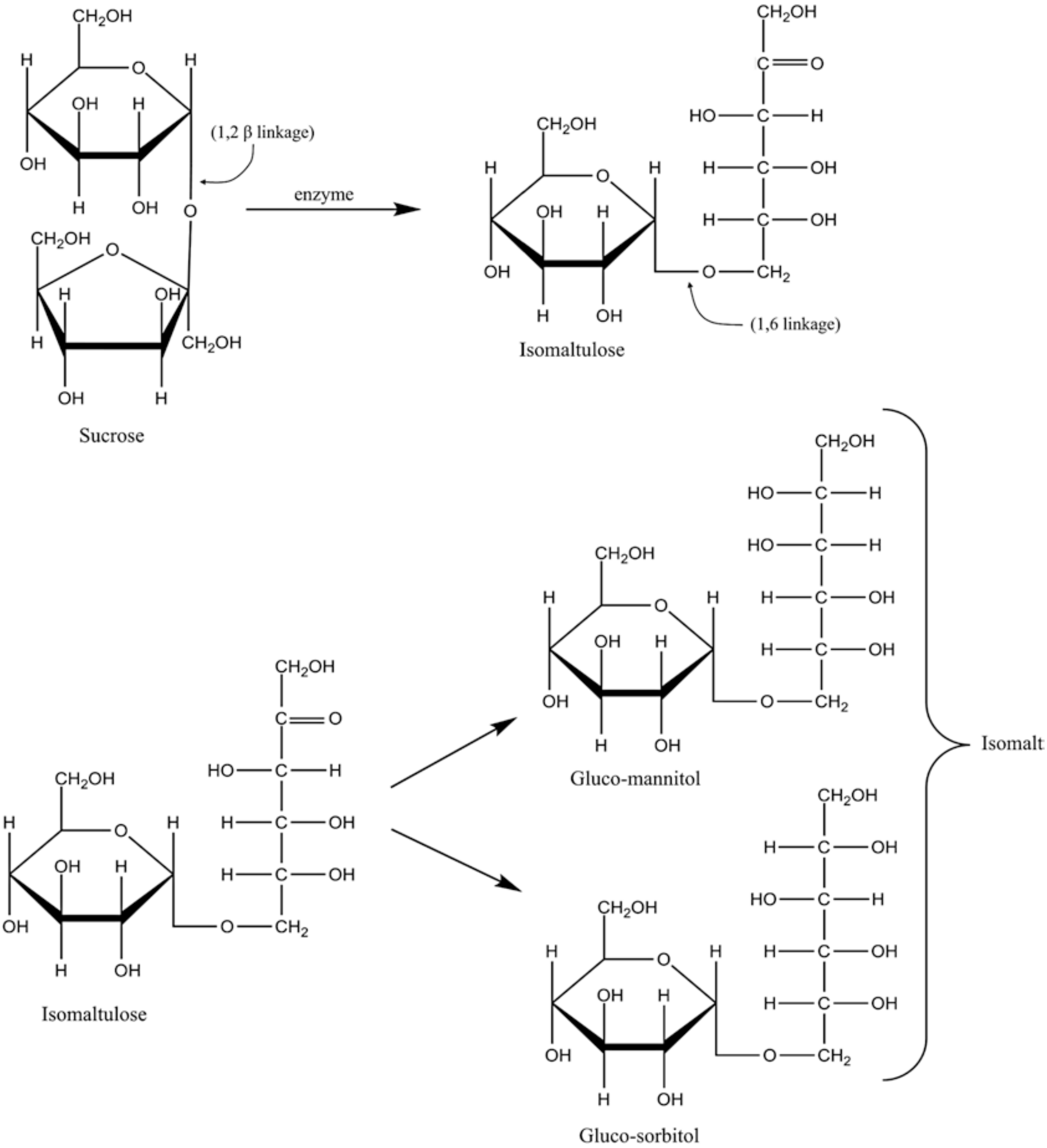

Figure 1.15 Conversion of sucrose to isomalt

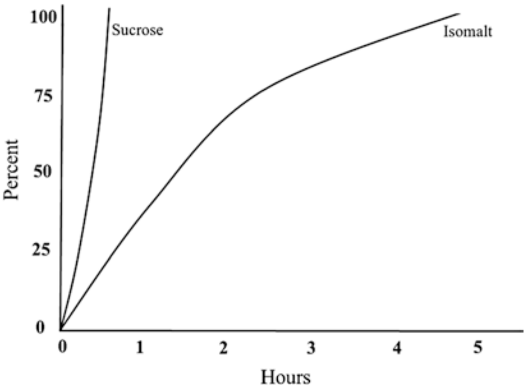

Figure 1.16 Hydrolysis of isomalt vs. sucrose in 1% HCL at 100 °C

(1-6)-D-mannitol). The reactions are shown in Figure 1.15.

Isomalt is a white, odorless, crystalline, nonhygroscopic substance. Many of its properties are similar to sucrose, which allows, in many applications, the direct substitution for sucrose. It is very stable and, because it is only half as sweet as sucrose, isomalt serves as an excellent bulking agent. A comparison of the stability of sucrose and isomalt in 1% HCL at 100 °C is shown in Figure 1.16. As seen, isomalt is more resistant to hydrolysis under acidic conditions than sucrose.

Because of its similar properties to sucrose, isomalt is often used as a direct sucrose replacement. For example, hard candies are often made with isomalt, with similar physical properties and shelf life as sucrose-based hard candies. Isomalt can also be used in sugar-free hard panning, giving a shell with similar crisp character as sucrose.

1.8.3.2 Maltitol

Maltitol is the product of hydrogenation of maltose, produced by hydrolysis of starch. Maltitol is used in confections as either a crystalline powder or as hydrogenated high maltose syrup (see below). Powdered maltitol is produced either by crystallizing from a maltitol syrup or by direct extrusion crystallization of the syrup. The former method produces maltitol powders of higher purity than the latter.

Refined crystalline maltitol has many similar properties as sucrose, including sweetness, solubility and low hygroscopicity. It may be used to replace sucrose in fondants and creams, chocolates and coatings, or hard-panned candy shells.

1.8.3.3 Lactitol

Lactitol, like mannitol, is produced by hydrogenation of its parent disaccharide, in this case lactose. Hydrogenation occurs at the glucose portion of the molecule. Lactitol is primarily found as a crystalline powder with high stability to both temperature and acid. Both lactitol and maltitol are sweeter than their parent disaccharide (Table 1.13).

Lactitol is not used widely in confections, but finds application in hard candy, hard-panned shell candy, and sugar-free chocolates and coatings.

1.8.4 Hydrogenated Starch Hydrolysate (HSH) and Maltitol Syrups

HSH syrups are manufactured by the hydrogenation of glucose syrups (or starch hydrolysates). HSH syrups are mixtures of various chain length polyols, with composition dependent on the type of glucose syrup used as the starting point. In the hydrogenation of glucose syrups, glucose is converted to sorbitol, maltose to maltitol and so on through the range of glucose polymers present in the glucose syrup (Figure 1.17). Analogous to glucose syrups, the composition of HSH syrups are described based on the chain length or degree of polymerization (DP) of the saccharides. Specifications will give the amounts of monosaccharide polyols (DP 1), disaccharide (DP 2), tri- to hexa- (DP 3–6), and over DP 6. Maltitol syrups are a subset of HSH, made by hydrogenating high-maltose syrup. They must contain a minimum of 50% maltitol (dry basis).

As with glucose syrups, HSH syrups have different properties when used in confections, dependent on the composition. HSH syrups with low average molecular weight provide enhanced humectancy and sweetness and are more hygroscopic than those with higher average molecular weight. However, HSH syrups with larger mole-

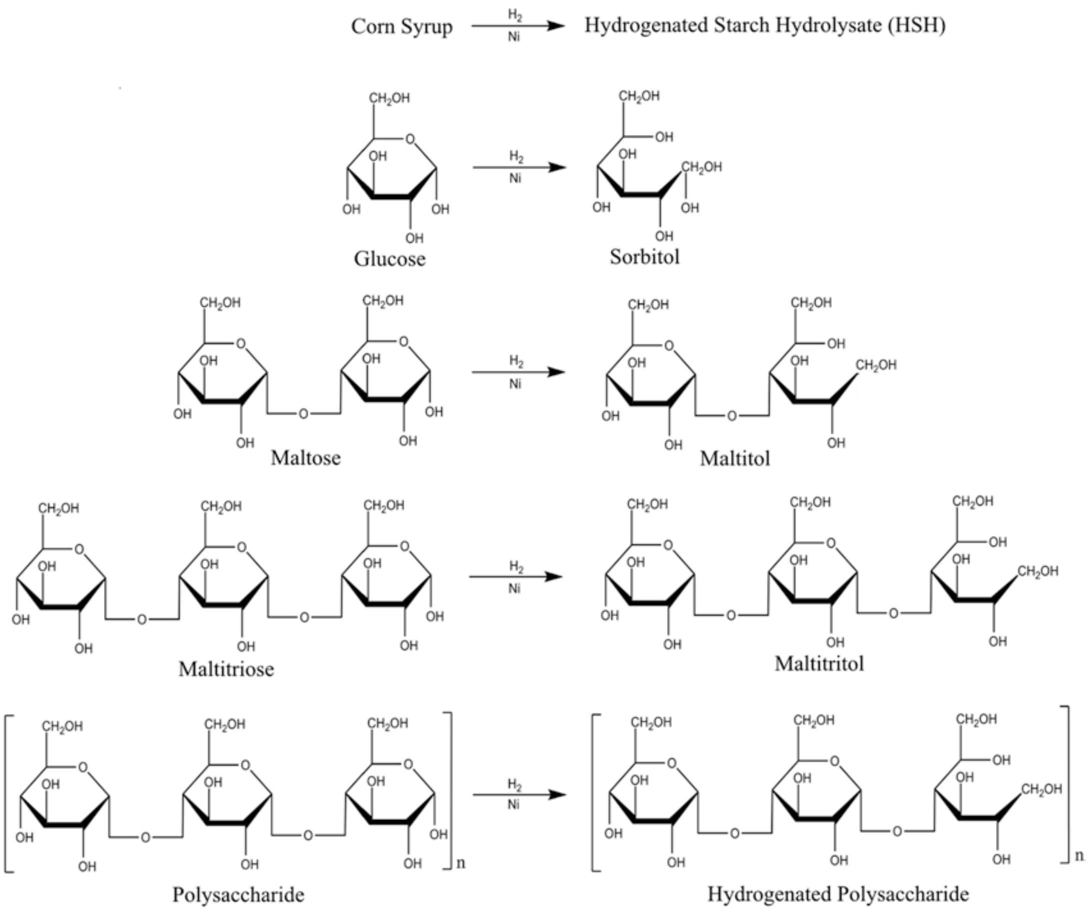

Figure 1.17 Catalytic hydrogenation of glucose syrup

cules provide enhanced viscosity and stability. During digestion or heating, particularly under acid conditions, HSH syrups may be hydrolyzed into glucose and sorbitol. The reducing groups formed will then participate in reactions that require reducing groups including fermentation, which could promote dental caries.

HSH syrups find wide application in confections. They are often used in the same manner as glucose syrup in sugar confections, to provide bulking capacity and for controlling crystallization. As such, they can be used in sugar-free versions of chewing gum, hard candy, gummies and jellies, fondants and creams, and caramels and taffy. In gum, for example, HSH can be used to moderate the recrystallization of sorbitol and to provide humectancy.

1.9 High Intensity Sweeteners

High intensity sweeteners are used with bulking agents that are less sweet than sucrose. A number of these sweeteners have been developed, including sucralose, aspartame, acesulfame-Potassium (Ace-K), alitame, thaumatin, neotame, and stevia, with new ones continually being studied. Reviews of these noncaloric sweeteners can be found in DuBois and Prakash (2012) and Pawar et al. (2013). Their use is often limited by regulatory status and/or limitations related to their physical properties. Fortunately, usage levels in confections are very low, less than 0.1%. Chemical structures of some high intensity sweeteners are shown in Figure 1.18.

1.9.1 Sucralose

Sucralose, or tricholorogalactosucrose (Figure 1.18), is 600 times as sweet as sucrose with a clean sweet taste with lingering sweetness in the aftertaste. It is a nonnutritive sweetener that is stable to acid hydrolysis. It is hygroscopic and if slightly moist at low pH, hydrolysis can occur. Its solubility in water at 20 °C is 283 g/L.

1.9.2 Aspartame

Aspartame, marketed as Nutrasweet®, is the methyl ester of the peptide aspartylphenylalanine (Figure 1.18). It has a sweet taste 180–200 times as intense as sucrose. Aspartame has a clean

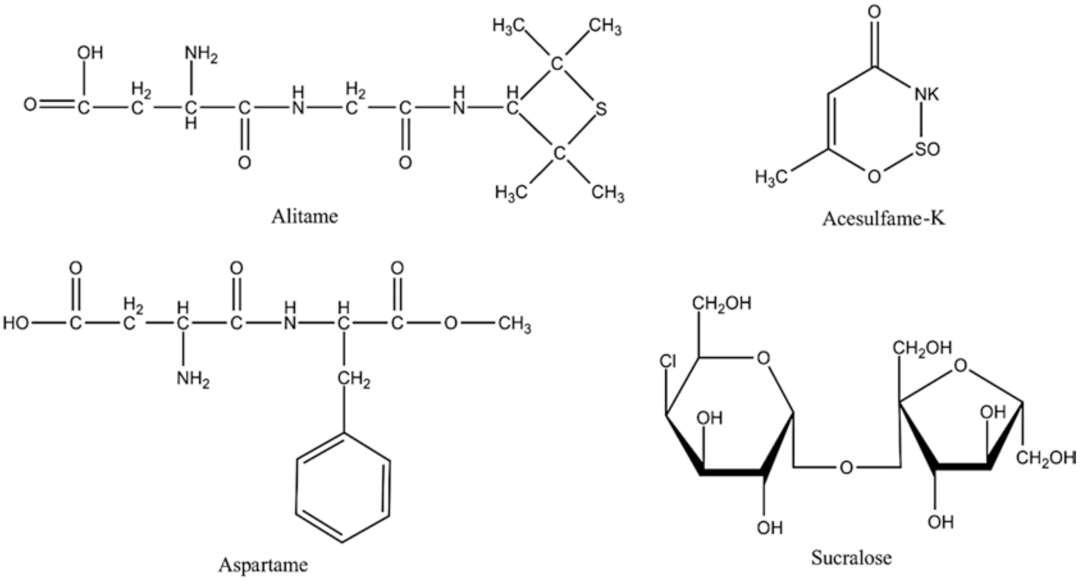

Figure 1.18 Structure of some high intensity sweeteners

Table 1.14 Solubility (%) of aspartame in water as affected by pH value

	Temperature (°C)		
	4.5	20	30
pH			
1.0	3.5	4.5	7.0
2.0	6.0	7.5	10.0
3.0	2.0	2.5	3.0
4.0	0.75	1.0	1.35
5.0	0.5	0.75	0.9

sweetness, with a sweet aftertaste. It has a low solubility (Table 1.14) and is not heat stable. Even at room temperature, it degrades into its component parts, including the amino acid phenylalanine, which some people cannot tolerate. This limits its usage in confections, due to the heat treatment required for most candies. Its primary use is in gum products, although, even in gum, deterioration of aspartame is of sufficient concern that significant efforts have gone into means of protecting it to retard or prevent its degradation. Although a nutritive sweetener, because of it low usage level, it contributes little to the caloric value of a product.

1.9.3 Acesulfame-Potassium

Acesulfame-K (Figure 1.18) is a nonnutritive sweetener, marketed under the trade name Sunette© and Sweet One©. Its sweet sensation is 200 times that of sucrose, with a bitter/metallic taste. Acesulfame-K is highly water-soluble and heat stable. At 0, 20 and 100 °C the solubility in water is 14, 27 and 130 g/100 ml, respectively. It has a synergy with other sweeteners and reduces some of their undesirable effects; thus, it has much promise when used in combination with other intense sweeteners.

Table 1.15 Solubility (%) of alitame in water as affected by pH

	Temperature (°C)				
	5	20	30	40	50
pH					
2.0	42	49	56	50	54
3.0	32	39	47	51	54
4.0	13	14	17	20	38
5.0	12	13	15	17	29
6.0	12	13	15	20	33
7.0	12	14	18	30	52
8.0	15	25	47	56	52

1.9.4 Alitame

Alitame is a dipeptide (Figure 1.18) with a clean sweet taste and sweetness approximately 2,000 times that of sucrose. Since it is partially metabolized, it contributes 1.4 cal/g, although because of the low usage level, its caloric contribution is negligible. It is stable to hydrolysis, but has potential for off-flavor development during storage. Alitame is fairly soluble in water, primarily at pH values below 3 and above 7 (Table 1.15).

1.9.5 Thaumatin or Talin

Thaumatin is a plant protein extract. It is a single chain polypeptide of 207 amino acids with 8 disulfide bonds and a molecular weight of 22,209. As with alitame, it is 2,000 times sweeter than sucrose. The sweet sensation has a slow onset and is long lasting with a licorice aftertaste. Its solubility at 20 °C is 60.0 g/100 ml. The stability toward heat is pH dependent. It is most stable at pH 2.7–6.0, with optimal stability at pH 2.8–3.0. In the United States, it is considered a flavor ingredient.

1.9.6 Neotame

Neotame is chemically similar to aspartame, but with a dimethylbutyl group attached to the amino group of the aspartic acid component. This modification causes neotame to be about 8,000 times sweeter than sucrose (about 400 times sweeter than aspartame), meaning that very low levels are needed for sweetening purposes. Neotame is also much more stable than aspartame. It is not used widely in confections at this time.

1.9.7 Stevia

The steviol glycosides, extracted from the stevia plant, are made up primarily of stevioside, rebaudoside A, and rebaudoside C. Stevioside is 250–300 times as sweet as sucrose, while rebaudoside A is 350–450 times sweeter. Commercial products based on stevia are primarily composed of rebaudoside A since it is the sweetest component with least bitterness. Rebaudoside A is separated from the stevia leaf extract through a crystallization refining operation. In some countries, stevia may be considered natural.

1.9.8 Luo Han Guo (Monk Fruit) Concentrates

The luo han guo fruit (often called Monk fruit) contains mogroside V, along with several mogrol glycosides, with varying degrees of sweetness. Mogroside V is about 250 times sweeter than sucrose. Commercial products are dried fruit juice concentrates with a sweetness potency of about 100. Because it is derived from the fruit itself, these dried concentrates can be considered natural.

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Physico-chemical Properties of Sweeteners in Confections

2

Sugars and other sweeteners are often the main components of a confection. Besides making them sweet, they also provide bulk to the candy. However, the physico-chemical properties of the sweeteners do more than just provide bulk. The physical characteristics of a candy, which include consistency, chewy or stretchy characteristics, melt-in-the-mouth behavior, flavor release, and many other properties, are dependent on the nature of the sweetener. For example, sucrose by itself can be turned into candies with completely different characteristics – rock candy and cotton candy – simply by how it is processed. Rock candy, a crystalline form of sucrose, has very little color or flavor and takes a long time to dissolve in the mouth. Cotton candy, on the other hand, is a glassy form of sucrose that has colors and flavors distributed throughout the candy and dissolves almost instantaneously when placed in the mouth. To make high quality candies, it is important that the confectioner understand the properties of sugars that lead to these completely different characteristics.

2.1 Sweetness

The sweetness of sugars is related to their chemical structure and its interaction with taste receptors on the tongue. A detailed discussion of the chemistry of sweetness is beyond the scope of this book, especially since this is still an active area of research; see Fernstrom et al. (2012) for a recent review of mechanisms of sweetness.

Because a wide range of sweeteners may be used in confections, a comparison of the relative sweetness of the different sweeteners is needed. Numerous sensory comparisons of the sweet taste sensations of different sweeteners have been put forth. One method compares the threshold value needed for the subject to detect and identify the taste sensation of the substance under study. The threshold values for glucose, sucrose and fructose are 0.7%, 0.3% and 0.2%, respectively. At these low concentrations, fructose has a greater sweet sensation than either sucrose or glucose.

In the isosweet technique, the concentration of the substance under study determines which is equal in taste sensation to a certain concentration of sucrose. For example, concentrations of 15.5% or 48.1% glucose are required to equal the sweet taste sensation of 10% and 40% sucrose, respectively. Thus, at 10% sucrose concentration, glucose is only 65% (10/15.5 × 100) as sweet, while at 40% sucrose concentration, glucose is 85% (40/48.1 × 100) as sweet. At higher concentration of sugars, the differences in degree of sweet taste sensation become less pronounced.

A third method for comparing sweetness is the relative sweetness scale, where a 10% sucrose concentration is given a sweetness value of 1 (or 100). The relative sweetness of any other sweetener is then based on the relative concentration of

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Table 2.1 Relative sweetness of sugars and other sweeteners (various sources)

Sweetener	Relative sweetness[a]
Fructose	1.3–1.5
Invert sugar	1.1–1.25
Sucrose	1.0
Xylitol	1.0
Maltitol	0.8–0.9
Maltitol syrup	0.7–0.8
Glucose	0.7
Glucose syrup (60 DE)	0.65
Sorbitol	0.5–0.6
Mannitol	0.5–0.6
Isomalt	0.5
Glucose syrup (43 DE)	0.45
Lactitol	0.4
Glucose syrup (36 DE)	0.3
Maltose	0.3–0.5
Maltodextrin	0.1–0.3
Lactose	0.15–0.25
Polydextrose	0

[a] Based on sweetness relative to 10% sucrose solution (given a value of 1)

that sugar that gives the equivalent sweet taste sensation. Table 2.1 summarizes relative sweetness values for some of the important sweeteners used in confections.

2.2 Viscosity

Viscosity of a fluid may be defined as the fluid's ability to move under shear, as when it is pumped, stirred, boiled, sprayed or swallowed, for example. For a low viscosity fluid, like water, only a relatively small force is needed to induce flow, whereas higher viscosity fluids require more force to generate the same extent of flow. In this sense, viscosity is an important term for process engineers in designing pumping systems and equipment. The size of a pump needed to transport invert sugar (low viscosity) is significantly less for an equivalent flow rate of low DE glucose syrup. As another example, the viscosity of engrossing syrup is a critical factor for sugar panning operators to ensure proper syrup coverage on candy pieces tumbling in the pan. If viscosity of the engrossing syrup is too high, the pieces tumbling in the pan will not be adequately covered, whereas thin engrossing syrup leaves a residue on the inside of the pan rather than coating the pieces. Furthermore, viscosity also has important ramifications in the sensory qualities of confections. Typically, more viscous syrups are considered to be thicker and have higher consistency (mouthfeel). For these reasons, a good understanding of viscosity and what factors affect viscosity is one of the most important concepts for a confectioner. A good source for more details on viscosity, and the entire field of fluid rheology, can be found in Steffe (1996).

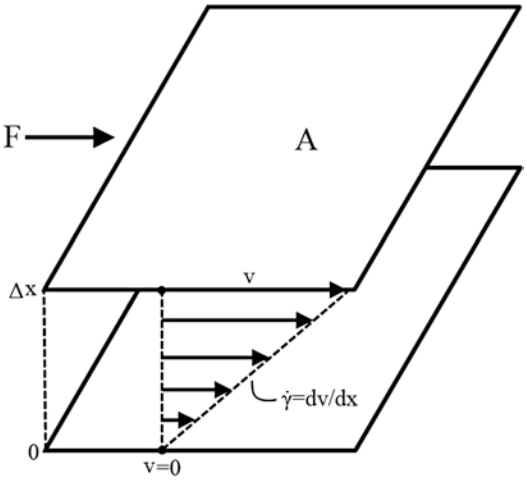

Figure 2.1 Shear flow between two flat plates (area *A*). The *top* plate is moving at velocity, v, while the *bottom* plate is stationary (v = 0)

Technically, viscosity for simple liquids (like water or sugar solutions) may be defined as the proportionality factor between the applied shearing force and the velocity gradient in the fluid caused by that shearing force. Imagine a fluid between two parallel plates of area A separated by distance x, as shown schematically in Figure 2.1. When a force, F, is applied to the top plate, it moves with a velocity, v, depending on the nature of the fluid (how the molecules respond to that applied force). If the bottom plate is stationary and there is no slip (fluid velocity at the bottom wall is 0), then the applied force creates a velocity gradient, dv/dx, from v at the moving plate to 0 at the bottom plate. The relationship between the applied force, or shear stress σ, and the velocity gradient, or shear rate $\dot{\gamma}$, is given mathematically as:

$$\sigma = F/A = \mu\dot{\gamma} = \mu\left(dv/dx\right) \tag{2.1}$$

where, the proportionality constant, μ, is the viscosity of the fluid between the plates. In practical terms, fluids with a higher viscosity require a greater amount of force to move at a certain speed.

When sugars are dissolved in water, the resulting syrups follow the general rule given by Equation 2.1. Fluids that behave according to Equation 2.1, where the shear stress is directly proportional to the applied shear rate, are called Newtonian fluids. A plot of shear stress versus shear rate gives a straight line, with the slope of the line being the Newtonian viscosity. The main characteristic that makes a Newtonian fluid is that the viscosity is the same regardless of how much shear is applied (how fast it is stirred or pumped). That is, shear stress increases in a direct proportion to the shear rate. Almost all sugar solutions, including glucose syrups, are Newtonian fluids. Oils (liquid fats) also belong to the Newtonian fluid category. Fluids are non-Newtonian when the apparent viscosity depends on the rate of shearing (see Section 15.5.3 for more details). For fluids with certain types of thickening agents (proteins, gums, etc.) and fluids with particulate matter, as found in fondant (aqueous) and chocolate (lipid-based), more complex relationships between shear rate and viscosity apply. Equation 2.1 no longer holds and more complex equations are necessary (see Section 15.5.3).

From a physical standpoint, viscosity is related to the ability of molecules to move past each other during shearing (mixing, pouring, pumping, swallowing, etc.). Factors that affect the ability of molecules to move relative to each other also affect viscosity. For Newtonian sugar solutions, the value of viscosity is dependent on the molecular weight of the sugar, the concentration and temperature. In general, high molecular weight sugars at high concentrations and low temperatures have high viscosity. Larger molecules generally have more difficulty moving past each other during shearing and therefore, exhibit higher viscosity. For example, lower DE glucose syrups with higher average molecular weight are significantly more viscous than the higher DE glucose syrups. Invert sugar, made up of two monosaccharides, has a very low viscosity. For comparison of the effects of molecular size, the viscosity of invert sugar and sucrose at 20 °C are shown in Figure 2.2. At equivalent weight concentrations, the viscosity of invert sugar is significantly less than that of sucrose due to the lower molecular weight.

The number of molecules present in solution, expressed as concentration, also impacts viscosity. The more molecules there are, higher concentration, the more likely those molecules are to impact each other and so the viscosity is higher. Viscosities of sucrose solutions at different concentrations are shown in Figure 2.3. Finally, when temperature increases, the kinetic energy of each molecule increases, which allows the molecules to move past each more readily, resulting in lower viscosity, also shown in Figure 2.3.

Glucose syrups, with a range of saccharide composition, behave as Newtonian fluids with a viscosity dependent on DE, as seen in Figure 2.4. Glucose syrups from different manufacturers, although they have the same DE, may have different viscosity due to the different saccharide distribution (and average molecular weight). However, the increase in viscosity with a decrease in DE of a glucose syrup can clearly be seen. This is evidenced by the relative ease of flow of 63 DE glucose syrup compared to 42 DE glucose syrup. Mageean et al. (1991) summarize viscosity data for a wide range of confectionery sweeteners.

2.3 Heat of Solution

When a sugar crystal dissolves in water, heat is evolved or absorbed depending on the nature of the process. Heat evolution is associated with the sugar molecules going from solid state to liquid state. The lattice enthalpy is the change in enthalpy as the sugar (and water when crystal hydrates exist) molecules dissociate from the crystal lattice. Solute-solute (endothermic,

Figure 2.2 Comparison of viscosity of sucrose and invert sugar at 20 °C (Data from Mageean et al. 1991)

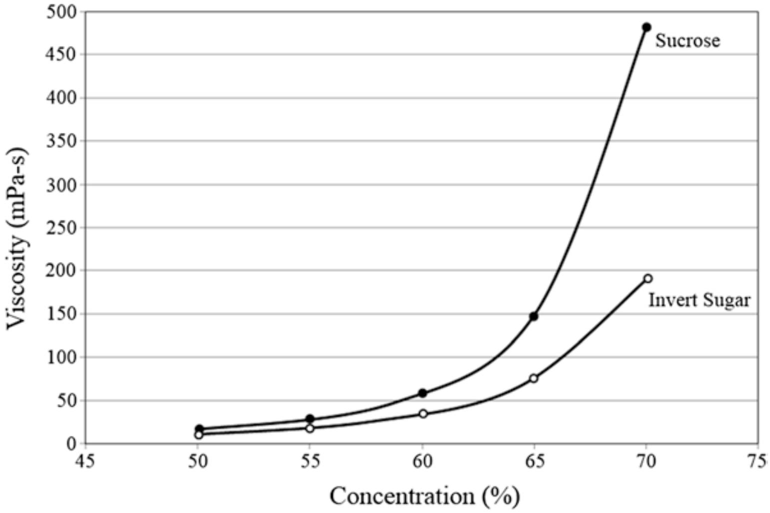

Figure 2.3 Dependence of sucrose viscosity on concentration and temperature (Data from Mageean et al. 1991)

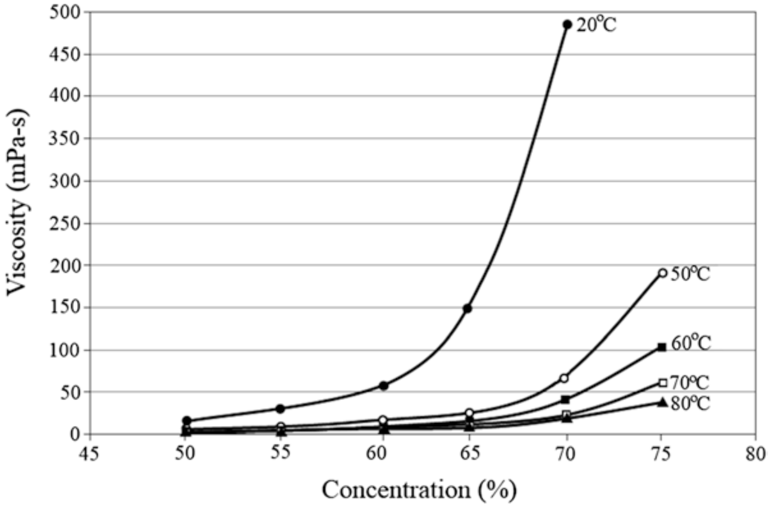

Figure 2.4 Dependence of glucose syrup viscosity (at 80% dry substance) on temperature (Data from Mageean et al. 1991)

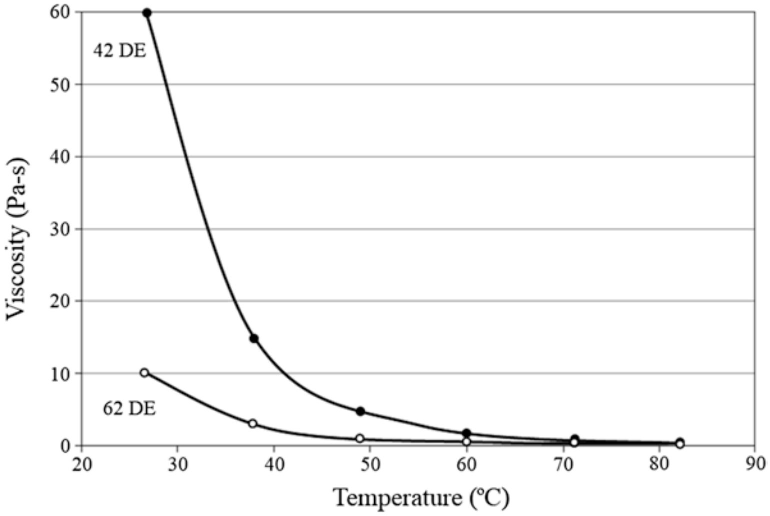

Table 2.2 Heats of solution (at 25 °C) for various crystalline sweeteners. By convention, a positive heat of solution indicates an endothermic (cooling) process

Sweetener	Molecular weight	Heat of solution (J/g)
Sucrose	342	18
Glucose anhydrous	182	60.6
Glucose monohydrate	182	105
Isomalt	344	39.3
Lactitol (monohydrate)	362	58.2
Maltitol	344	56.1
Sorbitol	182	111
Mannitol	182	121
Xylitol	152	153
Erythritol	122	180

Sources: Fritzsching (1995), Embuscado and Patil (2001), and Pancoast and Junk (1980)

removes heat from the environment) and, where pertinent, solvent-solvent (exothermic, adds heat to the environment) attractions must be broken in order for the crystal to dissolve. Once sugar molecules are dissociated from the lattice, there is an enthalpy term associated with solvation (or water hydration) of the sugar molecules (solute-solvent attraction), as they become part of the solution phase. This term is also exothermic, meaning heat is evolved into the solution. Finally, there is an enthalpy associated with dilution of the sugar molecules to the final concentration. By convention, the heat of solution for an endothermic process (cooling; removes heat) is positive while that for an exothermic process (warming; adds heat) is negative. Based on these energy principles, some crystals when dissolved in water cause the temperature to decrease (endothermic) while others cause temperature to increase (exothermic). For the most part, the sweeteners used in confections all give a cooling effect upon dissolution. Table 2.2 shows standard heats of solution for different confectionery ingredients. Many polyol crystals have a substantial cooling effect, which leads to some of the specific eating characteristics of sugar-free confections.

Sugar solids dissolving in water or saliva undergo complex changes as the molecules make the transition from a solid state to a diluted liquid state (Cammenga and Zielasko 1996). When a crystal dissolves, the endothermic change in lattice energy (latent heat) dominates the heat effect. However, when an amorphous glassy solid dissolves, there is no endothermic lattice energy, only an exothermic enthalpy of solvation (water hydration around the newly released sugar molecule). This means that when a piece of glassy hard candy dissolves in the mouth, there is a slight heating effect (not a cooling effect). Reiser et al. (1995) quotes a value of −16.9 kJ/mol for the heat of solution of a sucrose glass, whereas Knecht (1990) gives a value of −3.5 kcal/mol (8.4 kJ/mol). Cammenga and Zielasko (1996) found a heat of solution of −12.4 kJ/mol for dissolution of isomalt glass in water.

Note that when a concentrated sugar (or polyol) solution is diluted by addition of water (or saliva), this change in concentration, or dilution, is accompanied by an enthalpy change. This correlates to the third enthalpy term discussed above and is sometimes called heat of dilution. In most sugars and polyols, the heat of dilution is relatively small compared to the heat of solution (crystal dissolving). In sucrose, heat of dilution is generally about 1% of heat of solution (Reiser et al. 1995).

2.4 Specific Optical Rotation

When polarized light, or light vibrating in only one direction, passes through a sugar solution, the angle of polarization of that light is rotated depending on the type and concentration of the dissolved sugar. In the past, this property was used to measure the concentration of dissolved sugar with a polarimeter, although with better concentration measurement methods, the polarimeter method is rarely used any more.

A solution of glucose rotates a plane of polarized light to the right (clockwise), or in the *dextro*-rotary direction. It is this property of glucose that has led to it being called dextrose. Fructose, on the other hand, rotates light to the left, or in the *levo*-rotary direction (counter clockwise), which is why fructose is sometimes called levulose. Most of the sugars of concern in confectionery syrups, including sucrose, maltose and

Table 2.3 Specific optical rotation (Light source: D-line of Na) of various sugars at 20% concentration

Sweetener	Temperature (°C)	Optical rotation (degrees/dm)
Sucrose	20	+65.2
α-D-glucose	20	+53.0
Fructose	25	−91.4
Invert sugar	20	−20.4

Estimated from Mageean et al. (1991)

lactose, rotate light to the right. Since glucose, maltose and higher molecular weight glucose polymers all rotate polarized light to the right, glucose syrups have the same property.

The type of sugar, its concentration, temperature, and the wavelength and path length of light passing through the sugar solution all affect the measured optical rotation. Specific optical rotation is defined as the angle of rotation of polarized light of specified wavelength (the D line of sodium at 589.3 nm) passing a distance of 10 cm through a solution at 20 °C, as given by Equation 2.2.

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l * c} \tag{2.2}$$

Here, α is optical rotation, l is the path length of light, and c is concentration. Specific optical rotation of various sugars at 20% is given in Table 2.3.

Under standardized conditions, fructose rotates light farther to the left (−91.4°) than glucose rotates light to the right (+53.0°), so that invert sugar, the equimolar combination of glucose and fructose, has a slight left-handed optical rotation (−20.4°). Sucrose has a positive optical rotation (+65.2°). When it is hydrolyzed to form invert sugar, the equimolar mixture of glucose and fructose, the optical rotation switches from positive to negative. It is this “inversion” of the optical rotation from right to left that historically gave rise to name “invert sugar” upon complete hydrolysis of sucrose.

2.5 Refractive Index

Another optical property of solutions is refractive index. When you look at an object immersed in a pool of water, you know that the object is not really where it appears to be. As light passes from air into an aqueous solution, its direction is changed, or refracted, depending on the optical properties of the solution. This well-known change in path of a light beam when it goes from air into water is due to the difference in speed of light in the two materials. Refractive index of a material is generally given as the ratio of the speed of light in air (or technically, in vacuum) to the speed of light in the material. The refractive index of water at 20 °C is 1.3329 (relative to air, which is generally considered to have a refractive index of 1.0000 using sodium light as the source). In contrast, the refractive index for a saturated sugar solution (67 wt %) at 20 °C is 1.4581.

Each type of sugar exhibits a slightly different effect on refractive index, depending on its molecular properties. For pure sucrose, the change in refractive index with different concentration is shown in Figure 2.5. Based on this correlation, the measurement of refractive index can be used to quantify the concentration of sucrose in aqueous solution. That is, the exact concentration of a pure sucrose solution can be determined by measuring its refractive index. The concentration (from Figure 2.5) that corresponds to a measured refractive index is the concentration of the unknown solution. However, since refractive index changes with temperature, it should always be measured at a standard temperature of 20 °C (68 °F).

Also shown in Figure 2.5 is the effect of invert sugar on refractive index of solution. Fructose and glucose molecules have a slightly different refracting power than sucrose and thus, a different standard curve (from that of sucrose) must be used to calibrate the measurement of refractive index with concentration. There is a slightly different curve for each sugar and mixture of sugars. Figure 2.6 shows the refractive index curves for several different glucose syrups. Since glucose syrups can vary quite widely in saccharide composition, depending on manufacturer, process, and target DE, each glucose syrup will have a unique refractive index profile. The Corn Refiners Association, Inc. of the United States provides tabulated data for various glucose syrups, along with corrections for differences in DE and ash content (Corn Refiners Association 1990).

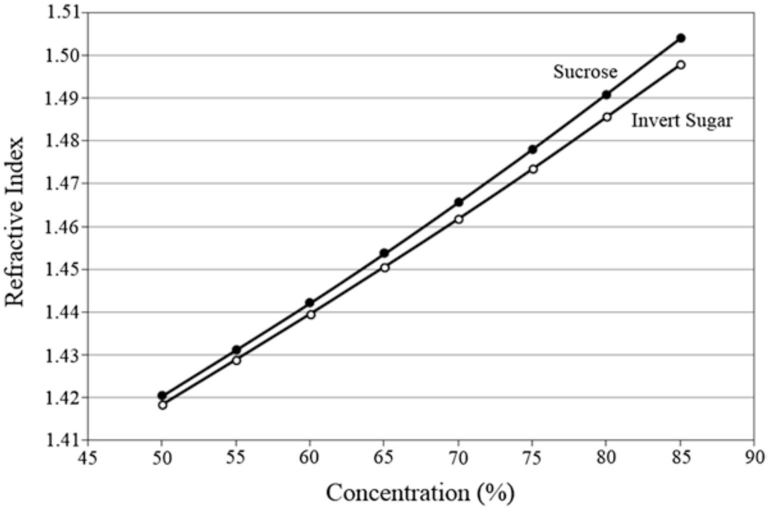

Figure 2.5 Refractive index of sucrose and invert sugar solutions at 20 °C (Data from Pancoast and Junk 1980)

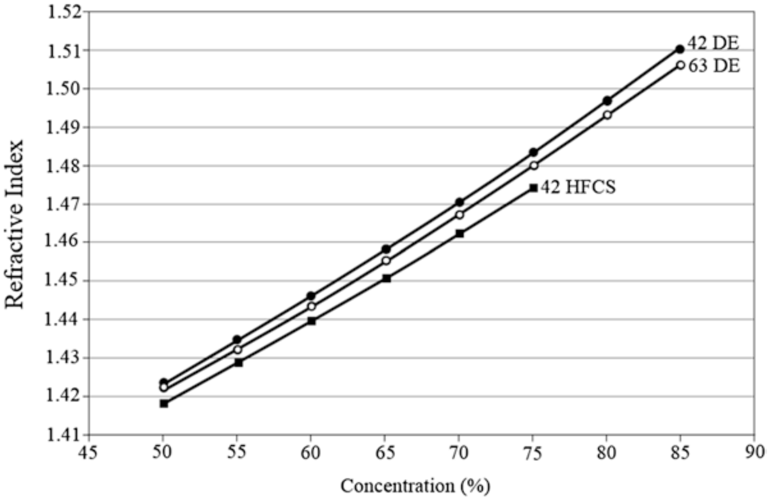

Figure 2.6 Refractive index curves at 20 °C for several glucose syrups: 42 DE (acid converted), 63 DE (dual converted) and 42 HFCS (high fructose corn syrup) (Data from Pancoast and Junk 1980)

Refractive index is measured with a refractometer, which is essentially a prism with a goniometer for measuring the angle of refraction of a beam of light as it passes through the solution. A small dab of sugar solution is placed on the prism and light is passed through the solution under controlled conditions. Refractive index is measured as the angle of refraction of the light between sugar solution and prism.

Refractometers read refractive index, which is directly related to the sugar concentration but the measured values depend on the types of sugars present in solution. However, refractometers used in the candy industry are typically calibrated to read sucrose concentration (weight % basis). That is, the refractive index is converted to a scale based on the equivalent concentration of sucrose based on the correlation in Figure 2.5. For a pure sucrose solution, the refractometer reading of concentration is accurate and reflects the true sucrose concentration. However, since each sugar reads a slightly different refractive index for a given concentration, the refractive index reading from a mixed sugar solution does not give the exact concentration of that sugar mixture in solution. To note this discrepancy between pure sucrose and complex sugar mixtures, the concentration reading from a refractometer is called degrees Brix (°Brix) rather than true concentration. That is, a pure sucrose solution with a concentration of 67% (weight basis) should read 67°Brix on the refractometer scale – the true concentration and °Brix give the same reading. If that pure sucrose solution is cooked to higher temperature so that some inversion of the sucrose takes place, the refractometer reading will be influenced by the presence of the glucose and fructose so that a °Brix reading of 90 no longer means that the sucrose concentration in that solution is 90%. A portion of the reading comes from the invert sugar, which has a different standard curve than sucrose (Figure 2.5).

The addition of glucose syrup to confectionery syrup leads to even more deviation between true concentration and °Brix. Correction factors for refractive index that allow determination of true concentration from °Brix are tabulated in various references (Pancoast and Junk 1980). The principle for correcting refractometer readings for binary blends of two sugars (denoted with different subscripts as 1 and 2) is given by Pancoast and Junk (1980) as:

$$n_D^{20} = \frac{\left(P_1 n_1 / S_1\right) + \left(P_2 n_2 / S_2\right)}{\left(P_1 / S_1 + P_2 / S_2\right)} \tag{2.3}$$

where, n_D^{20} is refractive index (at 20 °C for the D line of sodium light), P_1 and P_2 are percentages of the two sugar syrups being blended together, n_1 and n_2 are refractive indexes of each of the sugars being blended, and S_1 and S_2 are the dissolved solids (in percent) of each of the sugars.

For example, an equal mixture ($P_1 = P_2 = 50\%$) of saturated sucrose ($S_1 = 66.7\%$ with $n_1 = 1.4581$) with a 42 DE glucose syrup ($S_2 = 80\%$ and $n_2 = 1.49745$) is calculated from Equation 2.3 to have a refractive index of 1.47602. According to Table 2.4, the observed °Brix from a refractometer reading for the above mixture would be 74.0%. This reading would be in error due to the greater contribution of glucose syrup to the refractive index and thus, the actual dissolved solids concentration of the mixture would be less. The corrected dry solids content of this blended syrup would actually be 72.74%, so the correction factor would be −1.26%. Similar tables are available for mixtures of sucrose solutions with glucose syrups of different DE, high fructose corn syrup, dextrose solution, and invert sugar (see Pancoast and Junk 1980 for more details).

Table 2.4 Comparison of solids content of sucrose and 42 DE glucose syrup mixtures based on refractometer measurement

Sucrose solids (%)	Glucose syrup solids (%)	Solids content as measured[a] (%)	Actual solids content (%)
100	0	66.50	66.50
90	10	67.93	67.66
80	20	69.39	68.86
70	30	70.89	70.11
60	40	72.42	71.40
50	50	74.00	72.74
40	60	75.62	74.13
30	70	77.29	75.57
20	80	79.00	77.08
10	90	80.75	78.64
0	100	82.57	80.27

From Pancoast and Junk (1980)

[a] Brix – refractometer reading as if all dissolved solids were sucrose

Since the differences in solids content when using °Brix are generally small, within a percent or two at most, most confectioners choose to ignore these differences. Typically, as long as the product meets the desired specifications (hardness, etc.), the refractive index read as °Brix provides an adequate quality control tool in most circumstances.

2.6 Density/Specific Gravity

Density, or weight per unit volume, is an important property of sugar solutions since it provides a measure of how much sugar is dissolved in water. Because the molecular weight of sugar is so much greater than that of water, high concentration sugar syrups have higher density than water. Often, specific gravity, or the relative density of sugar syrup to water, is used to correlate against concentration. Since density of a material depends on the temperature at which it is measured, specific gravity must be specified at a

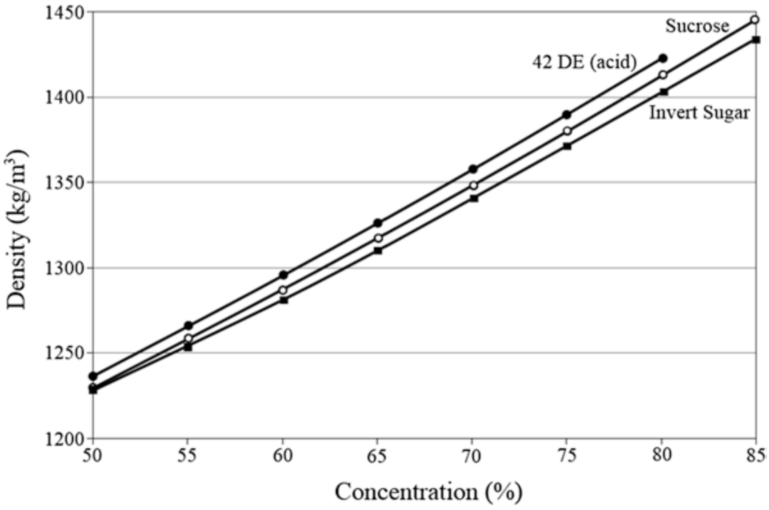

Figure 2.7 Density of various sugar solutions at 20°C (Data from Mageean et al. 1991)

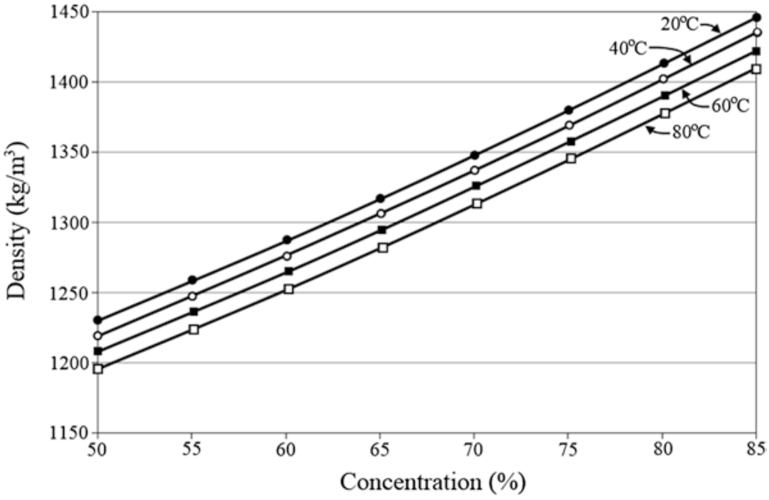

Figure 2.8 Effect of temperature on density of sucrose solutions (Data from Mageean et al. 1991)

certain temperature. It is most common to find specific gravity tables for sugar solutions where the density of sugar solution at 20 °C is referenced to the density of water at 4 °C, the temperature of maximum density for water (often taken as 1.000 g/mL although it is slightly lower than this). Figure 2.7 shows that density of sugar solutions increases as a function of concentration and that higher molecular weight sugars give solutions with higher density. Figure 2.8 shows the dependence of density of sucrose solutions on temperature. As expected, the density of sugar solutions decreases slightly as temperature increases. Data for specific gravity of a wide range of sugar solutions are tabulated in Pancoast and Junk (1980).

Specific gravity, or density, has in the past been typically measured by use of a hydrometer. A hydrometer is a floating glass tube with a weight in the bottom (i.e., mercury, lead shot) that is calibrated to read specific gravity along the stem. It is placed into the liquid and the level that the hydrometer sinks into the fluid is noted on the glass stem. Different hydrometers are used for fluids of different specific gravity. Electronic hydrometers, with continuous read-outs, now replace glass hydrometers in many applications. Continuous, in-line fluid density measurement is now common in many industries. Many in-line density meters are based on introduction of a vibrating element in the flow stream. The damping of the vibration is proportional to density. Alternatively, changes in ultrasonic vibrations can be used to measure density in-line as well.

The specific gravity of glucose (corn) syrups has long been of interest to the confectioner. The specific gravity of glucose syrups depends on both the saccharide composition and the water content. Typically, density, or specific gravity, of glucose syrups has been specified in units of degrees Baumé (°Bé), defined as (Pancoast and Junk 1980):

$$^{\circ}B\acute{e} = m - \frac{m}{SG_{15.6^{\circ}C}} \tag{2.4}$$

Here, m is a modulus (usually taken to be 145 – the ratio of the total volume of water displaced by the hydrometer to the volume displaced by the unit scale length of the hydrometer stem), and $SG_{15.6}$ is the true specific gravity at 15.6 °C (60 °F). According to Pancoast and Junk (1980), the corn refining industry reports “commercial Baumé” by adding 1 to the measured value at 15.6 °C (60 °F) in order to estimate the value at 37.8 °C (100 °F). The Corn Refiners Association bulletin E-8, the standard method for measurement of Baumé, indicates that measurements are made at 60 °C (140 °F) with an appropriate hydrometer (streamlines type, 145 modulus, standardized at 60 °F). The Baumé is then calculated as:

$$\begin{aligned}&\text{Baumé} = \text{Obs. }^{\circ}\text{Béat}\,60^{\circ}\text{C}\left(140^{\circ}\text{F}\right)\\&+1.00^{\circ}\,\text{Bé} + \text{Correction}\end{aligned} \tag{2.5}$$

The correction factor is required to correct for the difference in temperature of reading, 60 °C (140 °F) and temperature of hydrometer standardization, 15.56 °C (60 °F). The correction factor corrects for the relative thermal expansion of the hydrometer (glass) and the particular liquid.

More accurate (and simpler) determination of °Bé is accomplished by measuring refractive index to obtain total solids followed by calculation of °Bé from tables that correlate total solids with specific gravity. The Corn Refiners Association (Washington, DC) offers a software program (RI-DS) for correlating refractive index and dry substance based on the composition profile of a glucose syrup. That is, the relative weight of each saccharide (monsaccharides, disaccharide, trisaccharide and above) is input into the program. The output includes refractive index, dissolved solids, °Brix and commercial Baumé.

2.7 Boiling Point Elevation

One of the most important concepts in confectionery manufacture is the relationship between boiling temperature and final water content of the confection. The well-known boiling point elevation relationship is used to control the water content of a candy through control of the cook temperature (final boiling point).

The boiling point is directly related to the amount of water vapor in the air above the sugar syrup. The amount of water vapor that air can hold (given as water vapor pressure) increases with an increase in temperature (Table 2.5). It is this relationship between vapor pressure and temperature that defines the boiling point. Specifically, when the vapor pressure above a surface of water reaches the pressure of the ambient environment (atmospheric pressure), the water begins to boil. For normal atmospheric pressure (1 atmosphere = 14.7 psi absolute = 760 mm Hg = 29.92 in Hg = 101.3 kPa), the temperature where the saturation vapor pressure reaches atmospheric pressure occurs at 100 °C (212 °F). When atmospheric pressure changes, due to normal meteorological events (e.g., high or low pressure systems), the temperature at which water boils changes. Table 2.6 shows the relationship between atmospheric pressure and boiling temperature of water. When atmospheric pressure decreases below the standard value (101.3 kPa), the boiling temperature decreases; when pressure is greater than normal atmospheric pressure, the boiling temperature increases. Since water content of candy syrups is determined by cooking to a specified temperature, slight changes in atmospheric pressure can lead to changes in

Table 2.5 Temperature dependence of vapor pressure of pure water

Temperature (°C)	Vapor pressure (kPa)	Temperature (°C)	Vapor pressure (kPa)
20	2.34	65	25.00
25	3.17	70	31.16
30	4.24	75	38.54
35	5.62	80	47.34
40	7.38	85	57.81
45	9.58	90	70.09
50	12.33	95	84.51
55	15.74	100	101.32[a]
60	19.92		

Data from Handbook of Chemistry and Physics (1978)

[a]Normal atmospheric pressure

Table 2.6 Pressure dependence of boiling point of water

Pressure (kPa)	Boiling temperature (°C)	Pressure (kPa)	Boiling temperature (°C)
93.32	97.71	101.32[a]	100.00
94.66	98.11	102.66	100.37
95.99	98.49	103.99	100.73
97.32	98.88	105.32	101.09
98.66	99.26	106.66	101.44
99.99	99.63		

Data from Handbook of Chemistry and Physics (1978)

[a]Normal atmospheric pressure

final water content of the candy. Even the reduced atmospheric pressure at high elevations can cause changes in moisture content of a cooked candy.

The composition of an aqueous solution influences the boiling point of water through the colligative effect. Solute molecules influence the interactions among water molecules depending on the number of solute molecules and their size, as expressed by molality. This impacts the colligative properties, including boiling point and freezing point temperatures, water activity and osmotic pressure. Addition of smaller molecules affects these properties to a greater extent than addition of the same number of larger molecules. When equivalent weights of either glucose or sucrose are added to a sugar solution, there is a greater change in the colligative properties with the glucose solution than the sucrose solution due to smaller size of glucose molecules (higher number of moles for a given weight addition).

The interactions between solute and water molecules cause a decrease in the vapor pressure above the solution, which leads to an increase in the boiling point temperature (a boiling point elevation). The reduction in vapor pressure above a sugar solution means it must be heated to a higher temperature in order for the vapor pressure to be equal to the atmospheric pressure, the condition necessary for boiling to occur. Salts generally demonstrate an even greater effect on boiling point elevation than sugars owing to their lower molecular weight (higher molality at a given weight concentration).

When a sucrose solution is heated, it will first start to boil at the temperature associated with the boiling point for the given concentration and atmospheric pressure. For example, from Figure 2.9, the boiling point temperature for a sucrose solution saturated at room temperature (67%) is about 104.3 °C (220 °F). When that syrup begins to boil, water molecules are lost to the air and the solution becomes more concentrated. This higher concentration means that the boiling point temperature is now higher, according to Figure 2.9. Thus, as the sucrose solution continues to boil, both its concentration and boiling temperature increase according to the relationship shown in Figure 2.9. It is this relationship that allows the candy maker to know the concentration of sugar in a cooking syrup by simply measuring temperature. This is an important concept for confectioners since each candy must be cooked to the proper temperature to ensure the proper final water content in the product. However, it is important that the proper boiling point elevation curve is used for the specific sugar mixtures found in the candy formulation.

A significant body of literature exists giving boiling point elevations for various sugar solutions (see, for example, Pancoast and Junk 1980; Mageean et al. 1991; Starzak and Peacock 1998; Starzak and Mathlouthi 2006). However, there is considerable variation in the reported literature on boiling point elevation due to the difficulty in accurately measuring water content for different boiling temperatures. In part, this variation in the

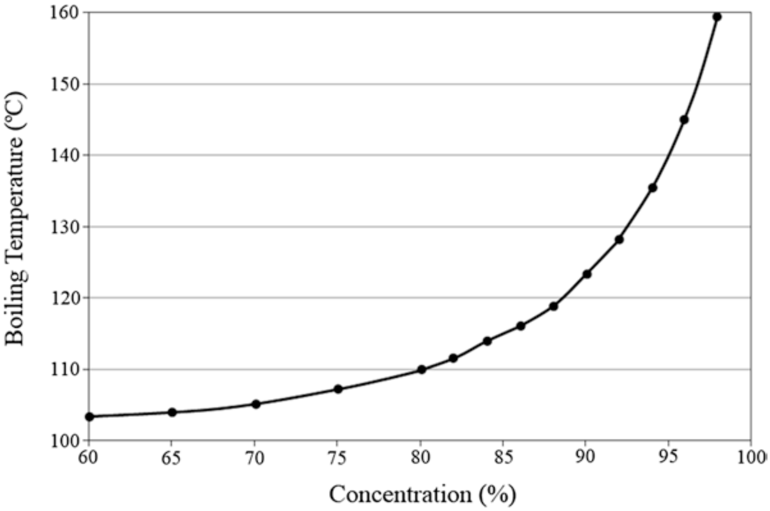

Figure 2.9 Effects of sucrose concentration on boiling point elevation of aqueous solutions (Data from Norrish 1967)

literature results from measurement difficulties and in part, it results from changes in the sugar syrup during heating. Once a sugar syrup has been cooked to the desired temperature, it must be cooled before water content can be measured. However, water is still evaporating from the syrup as it is cooling; therefore, unless great care is taken, the water content associated with a certain cook temperature generally underestimates the true water content since some of the moisture loss actually occurred during cooling. In addition, inversion of sucrose into fructose and glucose (with higher boiling point elevation) and decomposition of sugars (i.e., fructose) during cooking to high temperatures also introduces errors into boiling point measurements, especially at elevated temperatures (low moisture content). For these reasons, data provided in the literature must be used with caution.

Norrish (1967) evaluated boiling point elevation data for sugar solutions. Figure 2.9 shows the effects of pure sucrose on boiling point temperature of aqueous solutions at atmospheric pressure based on this study. Boiling point temperature increases from 100 °C (212 °F) with no sucrose to about 140.3 °C (284.5 °F) when sucrose reaches a concentration of 95% (by weight). When only 2% water remains (98% solids content), the boiling point temperature of a pure sucrose solution should be about 159.5 °C (319.1 °F). To document the disparity of data available in the literature, Cakebread (1972) states that the boiling point temperature for a 98% sucrose solution should be 137.7 °C (279.9 °F). This is over 20 °C less than the value from Jones (1959). For more details, this disparity in boiling point elevation (and other colligative properties) is discussed further in Starzak and Mathlouthi (2006) and Hartel et al. (2011).

Data in the literature for boiling point temperatures of other sugars of interest in confections are also inconsistent for the reasons noted above. Thus, all such data must be used with extreme caution. However, to demonstrate the influence of average molecular weight on boiling point elevation, Figure 2.10 shows data from the same study comparing glucose, sucrose, and 42 DE glucose syrup (Mageean et al. 1991). As average molecular weight increases, the boiling point temperature also increases, as expected based on colligative principles.

Figure 2.9 applies when atmospheric pressure is 101.3 kPa (760 mm Hg). Higher or lower pressures cause the boiling point temperature to change accordingly, with higher boiling temperatures at higher pressure and lower boiling temperatures under vacuum operation. Figure 2.11 shows the change in boiling point temperature of sucrose solutions for pressures slightly different than standard ambient pressure. Atmospheric pressure varies slightly due to natural weather

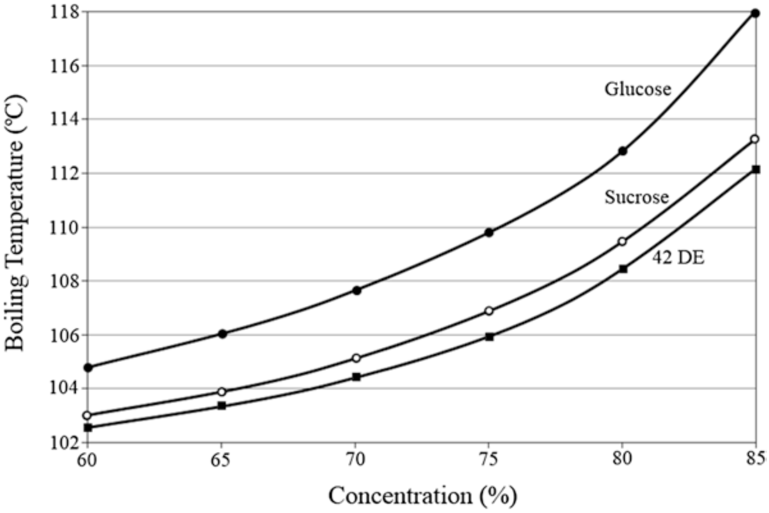

Figure 2.10 Comparison of boiling point temperatures for glucose, sucrose and 42 DE corn syrup (With permission Hartel et al. 2011)

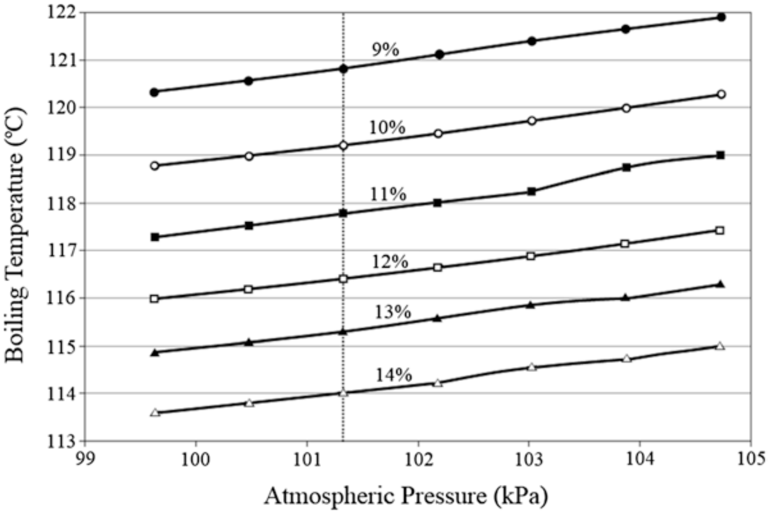

Figure 2.11 Effects of atmospheric pressure on boiling point temperature of pure sucrose solutions with water content from 9% to 14%. The *vertical line* represents normal atmospheric pressure (Data from Jeffery 2004)

phenomena (high or low pressure systems). A fluctuation of 3 kPa (22.5 mm Hg), from 99.8 kPa (748.75 mm Hg) to 102.8 kPa (771.25 mm Hg), well within normal daily variations in barometric pressure, would change the water content of a sugar syrup by approximately 0.5% if the same cook temperature was used. That is, a formulation cooked on a low pressure day could potentially have about 0.5% less water than the same formulation cooked on a high pressure day. Such a change in water content can potentially cause significant differences in texture, quality and shelf life of the confection, although most confectioners are not concerned with the effects of varying barometric pressure.

A similar effect on boiling point is observed with changes in altitude. Since atmospheric pressure decreases with increasing altitude, a manufacturing facility located at high elevation would have to compensate in cook temperature to mimic a product cooked at a facility at low elevation. In general, for each 304.8 m (1,000 ft) increase in altitude, there is an equivalent decrease in boiling point of about 1.1 °C (2 °F) (Stansell 1992). This can lead to an increase in water content on the order of 0.5%, again potentially leading to significant changes in texture and quality of a confection.

In commercial confectionery manufacturing, it is common to cook sugar syrups under vacuum[1] to reduce the effects of degradation reactions, including inversion and browning. Boiling point temperatures are significantly lowered by vacuum operation since a reduction in pressure means a lower vapor pressure is needed for boiling to occur. For example, boiling to 135 °C (275 °F) under a vacuum of 9.9 kPa absolute pressure (27″ Hg of vacuum) is about equivalent to boiling to 150 °C (302 °F) at atmospheric pressure, both conditions resulting in a water content of about 3%.

2.8 Solubility

An important aspect of sugars, salts, polyols and other confectionery ingredients is their ability to dissolve in water. When sugar crystals are added to water, the crystals dissolve until the dissolved molecules reach a maximum concentration, called the solubility or saturation concentration. The saturation concentration depends on the type of solute and the temperature of the solution. All sweeteners used in confections have what is known as a regular solubility curve, where the maximum concentration in solution increases as temperature goes up. In contrast, some salt molecules have an inverse solubility, where the maximum concentration in solution decreases as temperature increases. Such molecules, like calcium and magnesium bicarbonate, cause problems of scaling in hard waters due to this inverse solubility curve. As the temperature of hard water increases, the solubility concentration of these salts decreases until eventually they precipitate out.

When no further dissolution of sugar crystals occurs in solution, the sugar molecules in the liquid state are in thermodynamic equilibrium with the sugar molecules in the remaining crystals. There is no further net change in molecules from crystal to liquid or back again, although as with all equilibrium states, there is a continuous exchange of molecules between the two states (just no net change). Thermodynamically, equilibrium is defined as when the chemical potentials of the molecules in the two states are identical.

To measure solubility of a material in water, there are generally two approaches. The first approach is to add an overabundance of crystalline solids and allow the solution to mix, and crystals to dissolve, until no further changes in solution concentration occur. The maximum concentration attained is the saturation concentration, or solubility. The second approach is to prepare a high concentration solution (above the expected saturation concentration) and add a few seed crystals to initiate crystallization. As the crystals grow, solute molecules are removed from solution and the concentration of solute in the liquid phase decreases until equilibrium is attained. The final concentration of the liquid phase is the saturation concentration. Ideally, if a true equilibrium is attained and there are no kinetic constraints, both methods should give the same value of solubility concentration.

2.8.1 Solubility of Sugars

Sucrose exhibits a normal solubility curve, as shown in Figure 2.12, with saturation concentration increasing as temperature increases. At room temperature, sucrose is saturated at a concentration of about 67%, with that number increasing to over 80% at 90 °C (194 °F). Compared to sucrose, fructose is more soluble and lactose less soluble at all temperatures (Figure 2.13). Glucose, on the other hand has lower solubility than sucrose at temperatures less than about 50 °C (122 °F) and then higher solubility at higher temperatures.

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[1] Specification of a vacuum is based on an inverse pressure scale and is almost always given in units of inches of mercury (in Hg). That is, rather than increasing from absolute zero pressure, a vacuum scale increases numerically as pressure is reduced below atmospheric pressure. For example, since atmospheric pressure is 29.92 in Hg, a complete (absolute) vacuum would be 29.92 in Hg vacuum, equivalent to zero absolute pressure. A vacuum of 28 in Hg would then be the equivalent of an absolute pressure of 29.92 – 28 = 1.92 in Hg. Note: atmospheric pressure = 29.92 in Hg = 760 mm Hg = 101.325 kPa = 1.01325 bar = 14.696 psi (pounds per square inch).

Figure 2.12 Solubility of sucrose as function of temperature (Data from Mageean et al. 1991)

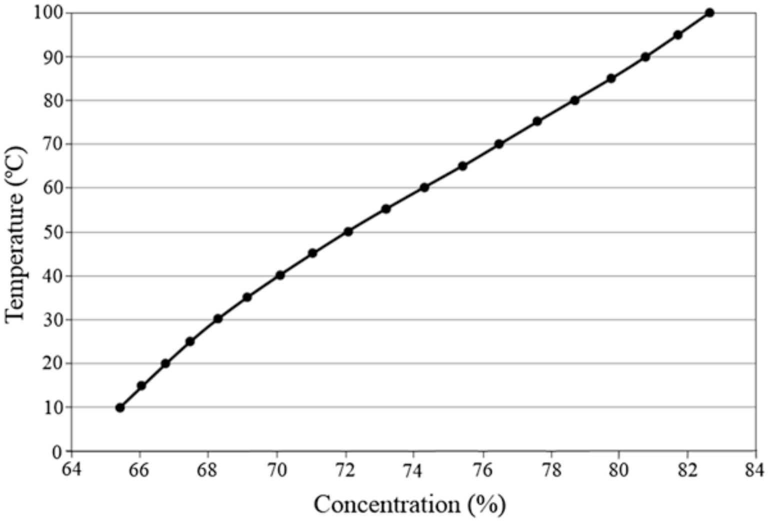
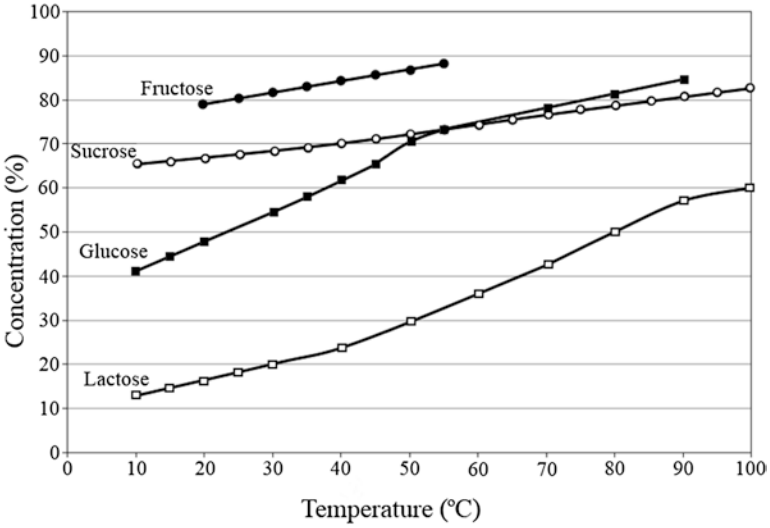


Figure 2.13 Solubility of various sugars (Data from Mageean et al. 1991)



In Figure 2.13, the solubility curves for glucose and lactose are not continuous, with breaks at about 50 °C (122 °F) and 93 °C (199.4 °F), respectively. These breakpoints represent the change from one anomer being the least soluble in solution to another. For example, glucose crystallizes as monohydrate at temperatures below about 50 °C and in an anhydrous form above that temperature. Glucose monohydrate is less soluble than the anhydrous form below 50 °C, so it is most likely to crystallize, whereas above 50 °C, the anhydrous form is the least soluble, so it is most likely to crystallize at elevated temperatures. Likewise, at temperatures less than 93 °C (199.4 °F), the alpha form of lactose is the least soluble, whereas at temperatures greater than 93 °C, the beta form of lactose is the least soluble. For this reason, to crystallize β lactose from solution requires crystallization temperatures greater than 93 °C.

2.8.2 Solubility of Polyols

Similar to the sugars, polyols show different solubilities in water depending on the molecular structure (and extent of hydrogen bonding with water). Figure 2.14 shows that maltitol is significantly

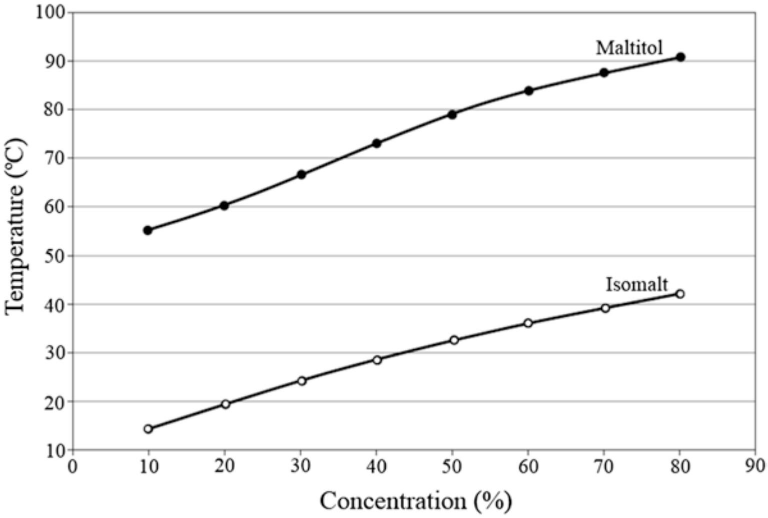


Figure 2.14 Solubility of isomalt (Data from Palatinit 1996) and maltitol (Data from Cammenga and Zielasko 1996) as function of temperature

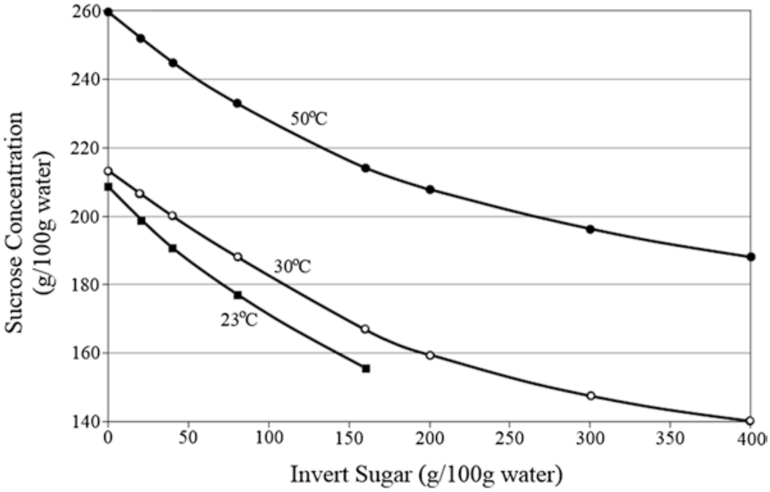


Figure 2.15 Solubility of sucrose in the presence of invert sugar (With permission Hartel et al. 2011)

more soluble than isomalt. The solubility concentration of maltitol at room temperature is about 60%, whereas isomalt is a lot less soluble at 24.5% at room temperature. The solubility concentrations of other polyols at room temperature include: γ sorbitol – 67.5%; mannitol – 18%; xylitol – 63%; lactitol – 55%; and erythritol – 37% (Embuscado and Patil 2001).

2.8.3 Solubility in Mixed Confectionery Syrups

When more than one sugar is dissolved in water, there is a competition for water molecules and the solubility concentration of each sugar decreases. For example, when invert sugar is mixed with sucrose, the maximum concentration of sucrose that can be dissolved decreases somewhat due to the presence of the glucose and fructose molecules. The more invert sugar present in solution, the lower the saturation concentration of sucrose at a given temperature, as seen in Figure 2.15. In this case, addition of 50 g invert sugar/100 g water causes about a 10% decrease in sucrose saturation concentration at room temperature, from 208.6 to 188 g sucrose/100 g water.

A similar situation applies for mixtures of sucrose and glucose syrup, where the presence of glucose syrup solids decreases the amount of

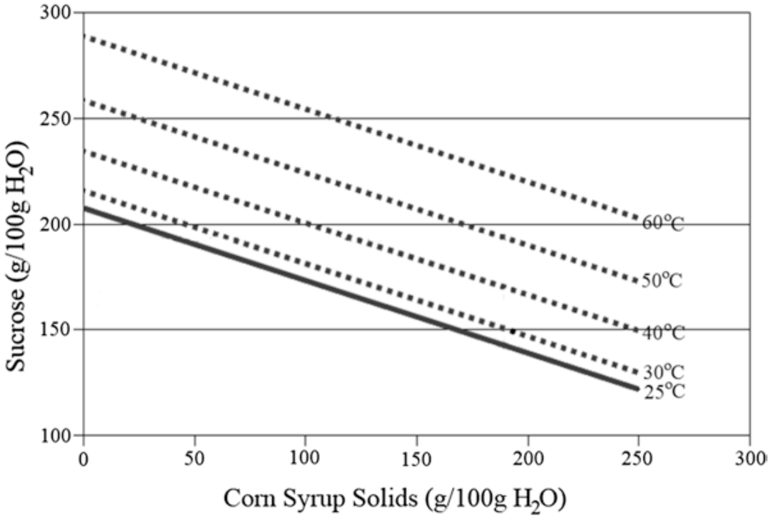


Figure 2.16 Effects of glucose syrup solids on sucrose solubility (Jonathon 2004). *Solids line* based on data, *dashed lines* based on projected curves

sucrose that can be dissolved in water. Figure 2.16 documents the decrease in solubility as the level of glucose syrup solids increases. Despite its importance in confections, very little quantitative data is available to show the effects of different glucose syrup solids (DE, saccharide distribution, etc.) on sucrose solubility. Fortunately, there appear to be minimal differences between the effects of invert sugar (Figure 2.15) and glucose syrup solids (Figure 2.16). In both cases, about 150/100 g water of the impurity give about the same solubility concentration (160 g sucrose/100 g water) at room temperature.

Despite the reduction in the amount of sucrose that can be dissolved to saturation in the presence of invert sugar or glucose syrup solids, the overall concentration of the mixed solution actually increases. That is, the total amount of dissolved sugars (including sucrose, invert and glucose solids) increases when different sugars are mixed together, as seen for mixtures of sucrose and glucose syrup solids in Figure 2.17. In this figure, as the percentage of glucose syrup solids in the mixture (on a solids basis) increases, the total amount of dissolved sugars, which includes sucrose and glucose syrup solids, increases. In this case, a 50:50 mixture of sucrose and glucose solids contains about 12% more dissolved solids than sucrose alone at saturation. The significance in this phenomenon is the increase in viscosity of this mixture and the reduction in water activity (making it more stable to microbial problems and drying out on storage).

Typically, the effects of other confectionery ingredients, besides other sugars, on the solubility concentration of sucrose are considered to be minimal. Ingredients such as hydrocolloids (starch, gelatin, pectin), fat, colors, flavors, etc., generally have little to no effect on the solubility of sugars. Some dairy ingredients, especially concentrated milk and whey products with high lactose content, can have a significant effect on the solubility of sucrose in water. For example, both glucose syrup and lactose present in a caramel formulation will act as doctoring agents to influence solubility and moderate sucrose crystallization.

When lactose levels are high, greater than the solubility of 16% in water at room temperature, then lactose becomes the sugar most likely to grain. In fact, in caramels made with high levels of milk or whey ingredients, lactose may be more of a problem for graining than sucrose due to its very low solubility (see Chapter 10 for more discussion on crystallization in caramel and fudge).

2.9 Glass Transition Temperature

The glass transition may be defined as the point where a fluid becomes sufficiently viscous to have the solid-like properties characteristic of a glass (or vice-versa, the temperature at which the

Figure 2.17 Total solids concentration for mixtures of sucrose and glucose syrup (42 DE) saturated with respect to sucrose. X-axis represents percent of glucose solids present on a solids basis (Data from Mageean et al. 1991)

viscosity of glass is reduced sufficiently to become fluid-like). Typically, viscosity values at this transition are around 10^{12} to 10^{14} Pa-s. The glass transition is usually taken as the mid-point temperature of the transition, which may extend over a wide range of temperatures (10 °C or more) depending on the composition of the material.

The glass transition temperature depends on the type of molecules forming the glass, the presence of solvent (water), and the addition of humectants (glycerol). In general, it is widely accepted that T_g increases approximately as the molecular weight of the glass-forming substance increases, although there are numerous exceptions to this rule. Table 2.7 compiles T_g values for various dry sweeteners (0% water) of importance to the confectionery industry. In general, monosaccharides have lower T_g than the disaccharides, but within each category, there is a range of T_g. For disaccharides, T_g varies from 65 to 70 °C (149–158 °F) for sucrose to 101 °C (213.8 °F) for lactose. The molecular nature of the sweetener determines T_g, not just their molecular weight.

Mixtures of sweeteners take on T_g values that fall between the values for the components in the mixture. For example, mixtures of sucrose and glucose syrup solids have T_g values that fall somewhere between that of pure sucrose and the glucose syrup being used, as seen in Table 2.8 for two types of glucose syrup solids. Mixtures of 42 DE glucose syrup solids with sucrose do not change the T_g of the mixture significantly until nearly half of the mixture is glucose syrup solids. The much higher molecular weight 20 DE syrup solids, with significantly higher T_g than sucrose, cause a substantial increase in T_g of the mixture even at relatively low levels. In contrast, mixtures of sucrose with high DE glucose syrup solids and/or invert sugar solids can cause a significant reduction in T_g of the mixture. For example,

Table 2.7 Glass transition temperatures for various sweeteners (in completely dry form) used in confections

Compound	T_g (°C)
Fructose	5–10
Glucose	31
Lactose	101
Maltose	87
Sucrose	62–70
Raffinose	70
Sorbitol	−9
Xylitol	−29
Maltitol	39
Isomalt	63.6
42 DE corn syrup solids	79
20 DE corn syrup solids	139
Polydextrose	90.8
Hydrogenated starch hydrolysate[a] (MW 504)	54.6
Hydrogenated starch hydrolysate[a] (MW 644)	75.0

With permission from Ergun et al. (2010)

[a] Maltitol syrups

Table 2.8 Glass transition temperatures (onset of calorimeter scan) for dry corn syrup – sucrose mixtures (less than 1% moisture)

Addition level (%)[a]	20 DE[b]	42 DE[b]
0	63.9 ± 1.4	63.9 ± 1.4
10	66.8 ± 0.4	64.1 ± 2.2
20	65.8 ± 2.6	66.9 ± 0.7
50	73.6 ± 3.0	69.1 ± 2.0
75	91.6 ± 1.3	70.9 ± 1.6
100	139.3 ± 0.8	79.0 ± 2.9

From Gabarra (1996)

[a] Addition on a dry solids basis (g corn syrup solids/100 g total solids)

[b] *DE* dextrose equivalent

invert sugar solids, an equimolar blend of glucose and fructose, would have a T_g about midway between each of the components, or about 17.5–20 °C (halfway between the values of 5–10 °C for fructose and 30 °C for glucose). Mixtures of sucrose with invert sugar solids would cause a significant reduction in T_g of the mixture. This reduced T_g will have significant effects on texture and shelf life (see Chapter 8 for a discussion on T_g and hard candy qualities).

The amount of water present in a confection has a huge impact on T_g, with even low levels (a few percent) of water causing a substantial (nearly 10 °C) decrease in T_g, as seen in Table 2.9. Slight changes in water content of a candy can have significant effects on T_g, thereby affecting texture and shelf life. Note that a sucrose solution with about 5.5% water has a T_g about room temperature, meaning that sucrose solutions with higher water content would have T_g less than room temperature and never attain the glassy state. Addition of 42 DE glucose syrup solids to the sucrose solution would raise T_g slightly (according to Table 2.8), meaning that the mixture with 5.5% moisture might now have T_g slightly above room temperature. To reiterate, the combination of sweeteners and water content determine T_g of the mixture. These values can be estimated based on composition but are best measured for the specific confection in question (Hartel et al. 2011).

Table 2.9 Effect of water content on glass transition temperature (T_g) of sucrose

Water content (%)	T_g (°C)
0	69
1	61
2	50
3	42
4	35
5	29

From Ergun et al. (2010)

The glass transition temperature, T_g, is important in many confectionery products since it is an indicator of texture and shelf stability. Confections with T_g above ambient temperature are in the glassy state, where molecular mobility is very low and the molecules are so tightly packed that they are no longer free to move about (either rotationally or translationally). Hard candy, brittles and some caramels fall into this category. These candies are relatively stable as long as they are maintained at conditions where T_g is greater than storage temperature and they are protected from moisture uptake (which lowers T_g). Confections with T_g below ambient temperature (not in the glassy state) have fluid-like characteristics dependent on how far T_g is below ambient temperature. For example, soft fluid confections (syrups, etc.) would have T_g well below 0 °C while firm, chewy candies (chewy nougat, taffy, etc.) have higher T_g (Ergun et al. 2010). As a general rule, candies with a higher T_g are harder and more brittle than those with lower T_g. In fact, the upper limit of T_g for the hardest sugar glass candies is probably between 50 and 60 °C (122 and 140 °F), although this has never been studied carefully. At such high T_g values, a sugar glass becomes sufficiently brittle that they are dangerous, where shards are sharp enough to pierce skin.

Detailed characteristics of the state of sugar in various confections are provided in Section 2.11 and in subsequent chapters on candy categories.

2.10 Crystallization Propensity

Controlling sugar crystallization is one of the most critical aspects of controlling texture, appearance, and overall quality of many confections. Thus, an understanding of the principles of crystallization as applied to confections is necessary. In general, there are three steps of importance to controlling crystallization: generating supersaturation, forming nuclei, and growth of those nuclei until phase equilibrium is attained. These principles apply for all sweeteners in confections, whether sucrose, glucose, lactose or polyols.

Once a sweetener solution has become supersaturated, the likelihood that it will crystallize depends on numerous parameters. These include the driving force (or supersaturation), the propensity of the specific molecule to crystallize, and the presence of inhibitors (doctoring agents). The driving force for crystallization is the difference between the actual concentration of the sweetener and the saturation concentration. In general, the larger that concentration driving force, the faster crystallization occurs (at least until the glass transition is approached). However, kinetic barriers may exist that retard or inhibit crystal formation. The primary kinetic barriers that impede crystallization of sugars in confections are (1) the reduced molecular mobility near and into the glassy state and (2) the inhibitory effects of doctoring agents commonly used to moderate crystallization in confections (Hartel et al. 2011).

When crystallization occurs, several steps are involved. First, nuclei must be formed from the supersaturated solution as liquid molecules organize into a crystalline (lattice) state. Once crystals have formed, they continue to grow as long as there is an available thermodynamic driving force. That is, as long as the sweetener concentration remains above the solubility concentration for the system (temperature and additives), crystals continue to grow. Since sugar molecules are being removed from the solution phase as crystals grow, the sugar concentration in the liquid phase decreases as crystallization proceeds until the endpoint at phase equilibrium when the solution concentration reaches the solubility concentration at that temperature. The rate of desupersaturation depends on the rate of nucleation and growth. Finally, once the maximal amount of crystals has been reached, there is a possibility of further changes in the crystal size distribution due to thermodynamic ripening mechanisms. That is, changes in the crystal size distribution can occur over time under certain conditions even though the total amount of crystals does not change.

2.10.1 Generating Supersaturation

In principle, there are three different methods to generate a supersaturated sugar solution: (1) removing water to concentrate the sugars, (2) cooling a concentrated sugar solution until concentration exceeds solubility at that temperature, and (3) adding a second solvent (an anti-solvent for sugar, like alcohol) in which the sugar is not soluble so that the sugar concentration in the mixed solvent is greater than the solubility concentration. To create a supersaturated solution in confections to promote graining, the solubility concentration must be exceeded in the process. This is usually accomplished through a combination of concentration (water removal) and cooling. In all cases, the effect is to increase the difference between the actual sugar concentration in solution and the saturation concentration.

Most confectionery processes involve cooking a dissolved sugar syrup to remove water and concentrate the sugars. As noted in previous sections, boiling a sucrose solution to remove water results in a continual increase in sucrose concentration at the same time the temperature rises due to the boiling point elevation effect. Interestingly, cooking a sucrose solution eventually results in a concentration above the solubility concentration. That is, as a sugar syrup is cooked, it goes from being undersaturated (crystals dissolve) to supersaturated (crystals can form) when the boiling point curve crosses the solubility. As seen in Figure 2.18 for pure sucrose solutions, this transition occurs at a temperature of about 112 °C (233.6 °F), when the concentration has reached about 85%. These values are slightly different when glucose syrups are added to the sugar mixture in confections due to their effects on both boiling point elevation (Section. 2.7) and sugar solubility (Section 2.8).

Cooling of the concentrated sugar syrup after reaching the desired cook temperature increases the supersaturation since the solubility concentration decreases as temperature decreases (see

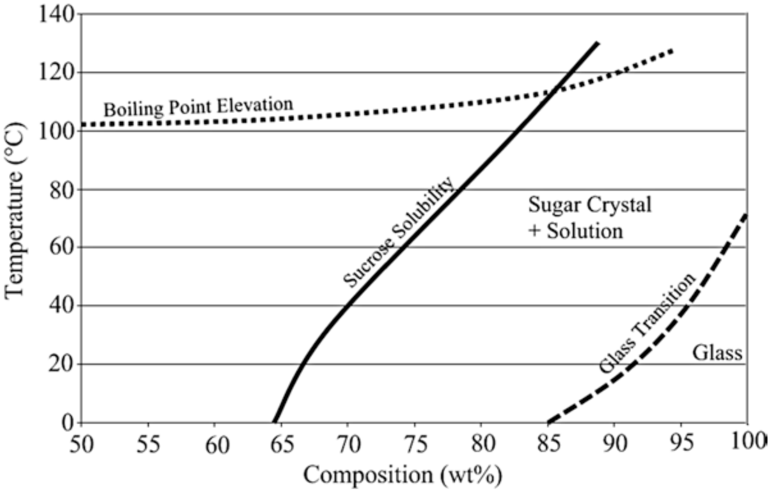


Figure 2.18 State diagram for sucrose (With permission Hartel et al. 2011)

Figure 2.12). Even though the sugar content of the candy batch does not change during cooling (unless some additional evaporation takes place), the supersaturation driving for crystallization increases because of the reduced solubility as temperature decreases.

Thus, during manufacture of many, if not most, confections, there is a period of time where the batch is likely to be supersaturated and will crystallize if conditions are appropriate. In confections where crystals are desired, both formulation factors and processing conditions are selected to promote graining, whereas in confections in which graining is to be avoided, formulation and processing conditions must be selected that minimize the potential for crystal formation (Hartel et al. 2011).

2.10.2 Crystallization

Crystallization involves two steps: nucleation and growth. Controlling crystallization of sweeteners in confections requires an understanding of each step of the process to obtain the desired crystalline content. Further, the competition between nucleation and growth for available supersaturation defines the final dispersion of crystals, whether there are fewer larger particles or numerous small crystals. Ultimately, the confectioner must be able control both formulation and manufacturing conditions to obtain the desired crystalline structure in the product for the desired textural and sensory properties.

2.10.2.1 Nucleation

Once a solution has become supersaturated, there is a driving force for the sugar molecules to come together to form a crystal nucleus. In all practical confectionery applications, some sort of particle or surface catalyzes nucleation, meaning that the first tiny bits of crystals, or embryos, form on the rough surfaces of microscopic particles (e.g., dust) or the walls of the vessel holding the solution. It is thought that interactions at these catalytic surfaces cause the molecules of the crystallizing species to organize in such a way that formation of the crystal lattice structure is enhanced. This process is often called heterogeneous nucleation since it involves an external component during nucleus formation (in contrast to homogeneous nucleation, which occurs in the absence of any external surface).

In principle, a sufficient number of molecules are needed to form a molecular cluster of sufficient size to become a stable nucleus. Homogeneous nucleation requires a larger number of molecules to form a stable cluster compared to heterogeneous nucleation since the surface present in the latter contributes some of the energy necessary to overcome the barrier to nucleus formation.

From thermodynamic considerations, two competing energy terms are relevant as a nucleus forms. For one, energy is needed to form a solution-crystal interface with a surface tension governed by the nature of the molecules. This energy term is proportional to the surface area of the nucleus being formed. For the other, energy is released when the molecules complete the phase transition, with energy being given up in the exothermic crystallization step (also known as the heat of crystallization). This energy term is proportional to mass (or volume) of the nucleus being formed. In the classical nucleation theory, these two energy terms are combined to yield measures of the energy barrier needed to overcome for nucleation to occur and the critical size of the nucleus at which point it becomes stable. The critical size of a molecular cluster that will form a stable nucleus is related to the molecular volume, the surface tension of the crystal-solution interface, the temperature, and the supersaturation. Smaller critical sizes are seen at higher supersaturations. For heterogeneous nucleation, the interaction between surface and crystallizing molecules also reduces the number of molecules needed to form a stable nucleus, thus catalyzing nucleation compared to the absence of that surface.

For further details on nucleation, see Hartel (2001) and Mullin (2001).

2.10.2.2 Growth

After a nucleus is formed, it starts to grow immediately and continues to do so as long as it is surrounded by a supersaturated solution. There are several steps that must occur before a sweetener molecule in solution contributes to crystal growth by becoming a unit in the crystal lattice. First, the sweetener molecule must move from the bulk solution to the crystal interface, either by convective motion or diffusion through the bulk. This mass transfer step is influenced by sweetener type (molecular weight) and concentration, temperature, viscosity (generally controlled by concentration and temperature), and agitation or stirring rate. At the interface between crystal lattice and solution, the sweetener molecule may need to be desolvated (lose any waters of hydration not carried into the lattice) before it begins the process of diffusing along the surface to find an appropriate site for incorporation into the lattice.

In a batch crystallization system, as may occur in a batch of fondant or fudge, once the crystals form during the nucleation step, the crystals grow and cause a decrease in the concentration of sugar in the remaining liquid phase. That is, the molecules that go into increasing the mass of crystals during growth leave the remaining liquid phase depleted in sugar. This decrease in solution concentration, or desupersaturation, continues until the solution concentration reaches the solubility point where it is saturated with sugar at that temperature (Figure 2.12 for pure sugar or Figure 2.16 for invert sugar/glucose syrup).

Further details on crystal growth can be found in Hartel (2001) and Mullin (2001).

2.10.2.3 Crystallization Rate

When a supersaturated solution crystallizes, both nucleation and growth take place. At first, nucleation dominates the process, especially when supersaturations are high, although growth starts almost immediately after the first nuclei are formed. Later in the crystallization process, when supersaturations have been decreased, growth becomes predominant. Nucleation may cease completely while the final supersaturation is relieved in crystal growth, up to the point where the solution reaches the saturation point at the solubility line (no remaining supersaturation). When the processes are combined like this, it is appropriate to talk about crystallization rate as the combined rate of the two steps.

The rate at which a sweetener crystallizes is influenced by the inherent chemical properties of the molecule, the presence of doctoring agents (inhibitors), and external operating conditions. The proper combination of these conditions allows control of graining to either prevent crystallization or to produce the desired crystalline phase (number, size, distribution, etc.).

The rate at which a sweetener crystallizes depends on numerous factors, including (1) the molecular nature, (2) the solubility concentration, (3) the effects of doctoring agents, and (4) the molecular mobility. In general, each sugar has its own inherent rate of crystallization, probably depending on the molecular interactions in the solution phase. The solubility concentration and its dependence on temperature also affect the rate of crystallization of a sweetener in a confectionery application. Materials with a high solubility, like fructose, generally do not crystallize very rapidly because it is difficult to generate high supersaturations without going to such high solids contents that molecular mobility is curtailed. In contrast, sweeteners with low solubility concentrations, like lactose, generally crystallize more readily because it is easy to generate high supersaturations.

Although most cooked confectionery sugar masses are supersaturated after cooking and cooling, and are thus prone to crystallizing, there is often a period of time in the supersaturated state before graining actually occurs. This time depends to some extent on the nature of the sweetener, or how easily the liquid molecules come together and rearrange into a crystal lattice. In other words, once a sugar syrup becomes supersaturated, the molecules require some time to organize and form into the crystal lattice, to nucleate. Some sweeteners, like mannitol and maltitol, are very easy to crystallize, whereas other sweeteners, like fructose, crystallize only very slowly. This is in part related to the nature of the molecules in solution and how it associates with other molecules (both of the same kind as well as of different kinds of molecules) (Bensouissi et al. 2010), but is also related to the relative supersaturations that can be developed in processing (temperature and concentration).

When a sweetener crystallizes, there is a phase change, liquid to solid that is accompanied by a release of latent heat. The kinetic energy inherent in liquid molecules is released as heat as they become more constrained in the crystal lattice. The amount of heat released depends on the type of sugar. Sucrose is reported to give off 2.5 kcal/mol at 25 °C and 8 kcal/mol at 60 °C (Knecht 1990). As long as this heat generation is removed quickly from the vicinity of the forming crystal, it has little effect on further crystallization. If, however, substantial crystal formation occurs over a very short time in an enclosed space (as can happen during crystallization of fondant), latent heat generation can cause the local temperature to increase, which in turn affects crystallization rate. For the most part, with the exception of fondant crystallization, the release of latent heat during sugar crystallization has minimal effect in confections.

Doctoring agents are added to confections to moderate crystallization of the primary sweetener. Glucose syrup and invert sugar play this role in sucrose-based confections. The same principle applies for the use of hydrogenated starch hydrolysate (see Section 1.1.2.14) to moderate sugar alcohol (i.e., maltitol, isomalt) crystallization in sugar-free applications. Doctoring agents may moderate crystallization in two ways. First, they may alter the solubility concentration of the sweetener and thereby, change the driving force for crystallization. But more importantly, they serve to interrupt the ability of sugar molecules to come together to form crystals. This inhibition arises primarily from the physical ability of the doctoring agent to impede the movement of the sugar molecules (especially at high viscosity), but may also result in part from chemical interactions (e.g., hydrogen bonding) between the different molecules.

In cases where rapid graining is desired to produce numerous small crystals, as in fondant and hard-panned sugar shells, it is important to minimize the presence of materials that inhibit crystallization. In fondant, the smallest amount of doctoring agent is used that will still give the desired texture. In this case, between 10% and 15% glucose syrup usually gives the desired fondant properties. The engrossing syrup for hard-panned candies should contain less than 1% glucose syrup or invert sugar to allow rapid and massive crystallization as each sugar layer is applied and dried. Although small amounts of glucose syrup can give a more pliable sugar shell, higher levels of glucose syrup do not provide the desired brittle shell by acting as a crystallization inhibitor.

On the other hand, in confections where graining is undesired, higher levels of doctoring agents are typically used. To avoid graining in hard candy and other amorphous sugar products, sufficient levels of inhibitors are needed.

Formulations containing as much as 50–60% glucose syrup, or more, may be needed in these confections. Crystallization rate is also impaired at conditions near the glass transition, due primarily to the lack of sufficient molecular mobility. If the molecules cannot move from place to place or rotate freely, they are unable to organize themselves into a crystal lattice and will not crystallize despite the large supersaturation.

By combining the principles of crystallization promotion and crystallization inhibition, a diagram of crystallization propensity (combined nucleation and growth) can be drawn for processing conditions (temperature and solution concentration). When a sugar solution of set concentration is cooled quickly from the cooking stage to a specific temperature and allowed to crystallize, there are several regions that characterize different aspects of crystallization. Figure 2.19 schematically shows these crystallization zones. When the hot sugar syrup is cooled just below the solubility point, crystallization rate is slow and sporadic. There is significant variability in crystallization onset in this region owing to the inconsistency of nucleation sites that promote formation of the first crystals at these relatively low driving forces.

At lower temperatures, approximately midway between the solubility and glass transition points, there is a region where crystallization occurs most consistently and rapidly (seen as the plateau in crystallization rate in Figure 2.19). The supersaturation driving force is sufficient to promote spontaneous and rapid crystallization, especially when accompanied by intense agitation, yet the mobility of the molecules is still sufficiently high to allow easy access into the crystal lattice. When crystallization is controlled within this region, the maximal number of crystals is formed. Because of the large number (and surface area) of crystals formed, each individual crystal remains small (ideally less than 15 μm), leaving the confection with a smooth texture. This is the ideal condition for graining of fondant, as discussed in more detail in Chapter 9.

At lower temperatures, below the plateau in crystallization rate, the rate of crystallization slows down and again becomes more sporadic. As the temperature decreases, the ability of the sugar molecules to migrate and rotate decreases in conjunction with the increase in solution viscosity as the system approaches the glass transition. Note that it is not really the increasing viscosity that "causes" this decrease in crystallization rate, it is the decrease in molecular mobility (which is what causes the higher viscosity). In this temperature region, formation of crystals is severely impeded, particularly as temperature is lowered.

Finally, if the hot candy syrup is cooled quickly through the crystallization zone to the point where temperature falls below the T_g value for that solution (sweetener types and water contents, as discussed in Section 2.9), the glassy state is attained. To avoid crystallization, the solution must be cooled faster than the time required for molecular organization and onset of crystallization. Once the candy mass is cooled below T_g, molecular mobility is so low that crystallization is unlikely to occur over the shelf life of the confection. This is the principle behind forming highly supersaturated products in the glassy state, or hard candies (see Chapter 8).

2.10.3 Seeding

Because of the difficulty in controlling the variable nature of nucleation, there are situations where the nucleation step can be avoided by seeding with the appropriate crystals to grain a batch. Fudge, creams, and nougat are examples of grained confections that might be seeded with crystals rather than crystallized within the process. Fondant is the most common seeding material for confections because of the small sugar crystals, but powdered sugar may be used if careful control of particle size is not critical. Either way, it is important that seeds be added at the appropriate point in the process, namely at the right temperature and water content, to gain the desired effect. Typical amount of seeding material needed to properly grain a confection is 5%.

When fondant is used to seed a batch of fudge or to make cast creams, the fondant must be

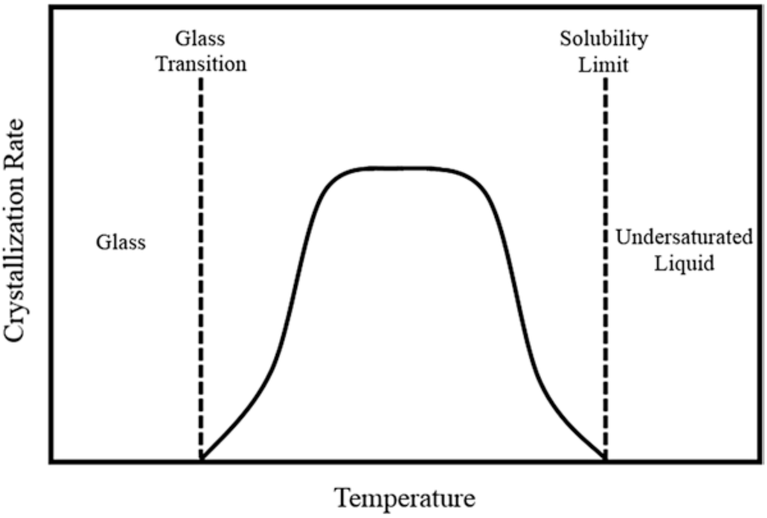


Figure 2.19 Regions of crystallization during cooling of a sugar syrup

introduced to the batch at the proper temperature (usually 160–180 °F/71–82 °C). Although warm temperatures are desired to ensure complete dispersion of the fondant into the candy batch, temperatures that are too warm result in dissolution of too many of the fondant crystals. Since the aim is to seed with the optimal number of seed crystals, any dissolution decreases the advantages of seeding. Further, if enough seed crystals dissolve completely away, regions of the confection may then nucleate to relieve the supersaturation. This results in scattered spots (usually whitish in color) randomly distributed throughout the candy.

2.11 State of Sugars in Confections

One way to distinguish different confections is in terms of the state of the sweetener. Table 2.10 distinguishes confectionery categories according to whether they are noncrystalline, partially crystalline or mostly crystalline. In liquid confections, the sugars are completely dissolved but viscosity is sufficiently low that the product can be poured. The sugar in amorphous and glassy confections is also completely in solution within the remaining water, but the viscosity is sufficiently high that mobility is limited. In glassy candies, like hard candy and brittles, the viscosity exceeds 10^{12} Pa-s so that T_g is greater than room temperature. A few candies, namely rock candy, tablets and lozenges, and powdered candies, are mostly crystalline with only minor amounts of other ingredients (colors, flavors, binders, lubricants, etc.). The category of partially-crystalline confections is quite broad and includes fudge, grained nougat and marshmallow, fondants and creams, and sugar-shelled candies. Partially-crystalline confections represent a difficult chal-

Table 2.10 Categorization of the states of sugars in sugar-based confections

Category	Examples
Noncrystalline	
Liquid	Syrup candies
	Gummies and jellies
Amorphous	Ungrained caramel, nougat, and marshmallow
	Salt water taffy
Glassy	Cotton candy
	Hard candy
	Brittles
Crystalline	Rock candy
	Candy powders
	Tablets
Partially crystalline	Grained (after dinner) mints
	Fondants and creams
	Grained caramel, nougat and marshmallow
	Fudge
	Hard and soft panned shell candy

lenge for confectioners since the relative contributions of sugars in each state must be carefully controlled to ensure the desired quality and shelf life.

The different states of sugar can be seen on a state diagram, as drawn for pure sucrose in Figure 2.18 (Hartel 2001). Similar diagrams can be developed for other sugars and for mixtures of sugars (as well as for polyols); however, state diagrams for other sweeteners and mixtures are not as common yet as that for sucrose. The state diagram can be used to understand the expected state of sugar during both processing and storage. To effectively use the state diagram to understand the state of sugar in confections, both thermodynamic (equilibrium) and kinetic aspects of crystallization must be understood.

Note that the state diagram in Figure 2.18 overlays equilibrium curves (boiling point elevation, solubility equilibrium of water and sugar) with a nonequilibrium boundary, the glass transition curve, indicating the distinction between glassy and fluid states. The regions delineated by the state diagram provide insight into what state of sugar can be expected at equilibrium, although the kinetic constraints noted earlier (doctoring agents and processing conditions during candy manufacture) also have a significant impact on the final state of sugar found in the candy (Hartel et al. 2011).

At high water content (and any temperature), the dissolved sugar molecules are in liquid form. This occurs when concentration is less than the solubility curve (see Section 2.8). If temperature of a dilute sugar syrup is increased to the boiling point temperature for that concentration, the syrup starts to boil. As boiling continues, the sugar concentration increases, causing a further increase in boiling point temperature. Thus, cooking a sugar syrup causes both temperature and total dissolved sugar concentration to increase according to the boiling point elevation curve (assumes an equilibrium is maintained between solution and vapor – a decent assumption for all but the most rapid cooking processes).

When the concentration of sugar exceeds the solubility curve at a given temperature, crystallization can occur. As noted previously, sucrose exhibits a unique characteristic where the boiling point elevation curve crosses the solubility curve (see the upper right quadrant of the state diagram in Figure 2.18). This phenomenon means that sucrose crystals can form during cooking under the right conditions (i.e., very slow – usually batch – cooking and limited doctoring agents to inhibit crystallization). A pure sucrose syrup cooked slowly is likely to crystallize even as it continues to boil. It is for this reason – to prevent premature crystallization – that candy makers rinse the inner kettle surface at the syrup line when making batches of grained mints and fondant, which are highly sensitive to graining during cooking.

The state diagram can be used to "follow" a candy manufacturing process to help better understand what state the sugar might be expected to take. This approach will be used throughout the various chapters in this book as appropriate.

2.11.1 Crystal or Glass

In a crystal, the sugar molecules are organized in a uniform, repeating lattice structure dependent on the lowest-energy molecular interactions. Crystallization is generally considered an exclusionary process; that is, when a crystal grows slowly, effectively all other molecules besides the sucrose are expelled from the lattice. In contrast to the ordered nature of the crystal lattice, the molecules of a sugar glass are randomly "frozen" together in space due to the rapid cooling of a concentrated solution. Figure 2.20 is a highly schematic attempt to show the difference in molecular arrangement between a crystal and a glass, being highly ordered and random, respectively.

The sugars in the different states have different physical characteristics and this leads to the differences in the characteristics of candy products. A sugar glass (e.g., hard candy) is able to incorporate other molecules (i.e., colors and flavors) since the sugar molecules are only randomly "frozen" together. This allows a hard candy to have colors and flavors uniformly dispersed throughout, and which are released con-

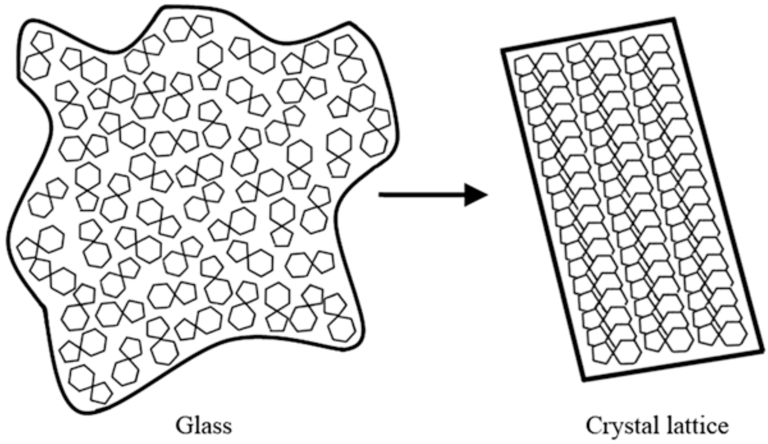


Figure 2.20 Schematic molecular arrangement of sugar molecules in a crystal and a glass

tinuously as the product is consumed. In contrast, the sugar crystal does not allow incorporation of other molecules, except in small amounts, so the majority of the colors and flavors of rock candy are contained on the surfaces of the crystals or in the small gap between individual crystals. Dissolution rates in the mouth are also different between glass and crystal. Since the molecules in the sugar crystal are tightly bonded to their neighbors, it is more difficult for molecules in crystalline form to dissolve. In glasses, the molecules are easily released from their neighbors due to the random organization and thus, a sugar glass dissolves much more readily in the mouth than a sugar crystal (assuming the same surface area).

Two essentially pure sucrose candies in different states, cotton candy and rock candy, clarify these relationships between making a sugar crystal or a glass. Note that the other sweeteners used in confections behave in a similar manner, albeit with slightly different parameters associated with crystallization and glass formation.

2.11.2 Cotton Candy

When flavored and colored sucrose crystals are melted at temperatures above 190 °C (374 °F), spun into thin fibers (or floss) and cooled rapidly, the result is cotton candy. A favorite at fairs, a cone of cotton candy is a glassy sugar matrix that has been spun into a fine floss and wrapped around a paper stick.

The starting point for cotton candy is essentially fine-granulated table sugar that has been coated with the desired colors and flavors. This powder is poured into the center of a cotton candy machine, often called a spinner. A heater in the center of the unit serves to melt the sugar as it spins, forming a liquid melt of colored and flavored sugar. The liquid sugar melt is forced through small holes on the periphery of the spinner by centrifugal force and a stream of sugar melt exits the spinner. As the liquid melt contacts ambient air, it is cooled very quickly so that the liquid melt immediately turns into a sugar glass in the form of fine strands, or floss. Since T_g for pure sucrose is over 65 °C (149 °F), the rapid cooling results in formation of a glass, rather than recrystallization of the sucrose.

Cotton candy is comprised of a series of fine threads of sugar glass or floss with colors and flavors uniformly dispersed throughout the glassy matrix. This high surface area of a glassy matrix is what allows cotton candy to “melt” in the mouth. Really, cotton candy simply dissolves quite rapidly due to the high surface area. But this same high surface area makes cotton candy highly unstable when exposed to normal air conditions, so that shelf life is short unless sealed tightly in a moisture barrier package. The high surface area provides an opportunity for rapid sorption of water from the environment, which leads to rapid recrystallization since no doctoring agents are added to inhibit crystallization (as would be used in the case of hard candy). Cotton candy exposed to the atmosphere lasts only a few hours (or less on a really humid day) before it begins to collapse as the sugar recrystallizes. When the sugar crystallizes, the colors and flavors are concentrated, which leads to a change in appearance. Regions of bright color appear as the dyes become concentrated in a localized region (excluded from the sugar crystals). This phenomenon also can be seen when the candy is eaten, leaving a ring of saliva around the point of consumption. The moisture in the saliva dissolves the sugar glass and recrystallization is rapid. As collapse occurs, the volume occupied by the fine threads of cotton candy also decreases and the cone shrinks in size.

2.11.2.1 Rock Candy

The simplest candy form of crystallized sucrose is rock candy. Rock candy can be found either as individual clusters of crystals sold in a box, as swizzle sticks, where the crystals are attached to a stick for sweetening a drink (e.g., tea), or as rock candy on a string. In some cultures, large individual sugar crystals are grown for direct consumption.

Traditionally, rock candy is made on a relatively small scale in a batch process. Granulated sucrose is dissolved in warm water, about 60–70 °C (140–158 °F) to a concentration around 70%. At this temperature, the solution is still below the solubility concentration for sucrose. The sugar syrup is then removed from the heat and allowed to cool, typically to room temperature. As the solution cools, it becomes supersaturated since the solubility of sucrose is lower at room temperature (only 67%). To promote crystal formation, either a stick or a string is inserted into the solution and crystals form preferentially on the nucleation sites provided by this foreign material. To optimize the growth of sugar crystals on the stick, the correct concentrations (supersaturations) must be used. If concentration is too high, the solution is too supersaturated, and nucleation will occur randomly throughout the solution, not just on the stick. Numerous crystals will be formed and they will remain small, with too few formed on the stick. On the other hand, if concentration is too low, very few nuclei will be formed and they will grow very slowly. Although good rock candy will be formed, the time required will be excessive. Thus, control of concentration is important in rock candy manufacture – it must be high enough to get fast growth but low enough that extraneous nucleation is not a problem.

In comparison to cotton candy, rock candy has an extended shelf life due to the stability of the sugar crystals. Crystalline sugar does not pick up moisture from the environment very readily. At low relative humidity, water vapor molecules in the air adsorb to the surface of the crystal, but the amount of water that can adsorb is based on the available hydrogen bonding sites on the surface of the crystal. The number of such sites is limited, so at relative humidity less than about 75%, there is very little increase in water content of rock candy (or any crystalline sucrose product). At slightly higher relative humidity (above 85%), though, there is sufficient water at the surface of the crystal to actually start dissolving the surface layers. The deliquescent point, or the point where a solid adsorbs sufficient water to become a solution, occurs when relative humidity reaches 86% for sucrose. At this point, the sucrose crystal dissolves, leaving a sucrose syrup.

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Water

3

Although water is not the primary ingredient in most candies, it plays a very important role in manufacturing, product quality, and shelf life (Ergun et al. 2010). Water interacts in confections through its ability to form hydrogen bonds with sugars and other confectionery components. As noted in previous chapters, these interactions have significant effects on such properties as boiling point elevation and water activity, two important aspects of candy manufacture and stability.

Water is introduced in many of the ingredients (i.e., glucose syrup, dairy ingredients, etc.) and, often, additional water is added to enhance process operations. In most cases, excess water is added to ensure adequate dissolution of granulated sugar and/or proper dispersion of ingredients into a homogeneous mixture. The starting sugar syrup is then cooked to the desired temperature to boil off excess water, with the end cook temperature denoting the final water content according to the boiling point elevation curve (see Section 2.7). Candies cooked to higher temperatures have lower water contents. If the water content is incorrect for the type of candy, it will be either too soft or too hard.

During storage, water plays an important role in quality and shelf life. Most, if not all, confections are not at thermodynamic equilibrium after they are made, meaning that they change according to the governing thermodynamic laws controlling the components of the confection. After manufacture, confections interact with their environment, either giving up moisture to the air or picking up moisture when humidity is high. Even when sealed in a moisture barrier package, interactions between the candy and headspace of the package can cause moisture changes that affect quality. Furthermore, moisture migration between elements of a multi-domain confection (e.g., cookie and caramel) can occur during storage, which can quickly lead to undesirable changes in candy characteristics.

Temperature changes during storage, as might normally occur from day to night or transport truck to retail outlet, also can cause significant changes in water balance in a confection. The amount of water that air can hold varies with temperature. As temperature increases, air can hold more moisture, so water migrates from the confection into the air. When temperature decreases again, air can hold less moisture and water attempts to migrate back into the confection. The result can often be significant changes in moisture profile and product quality deterioration with temperature fluctuations.

For these reasons, understanding what happens to water during manufacture and storage of confections is an important concern to the candy maker. Despite not being present at high levels, water is arguably one of the most important ingredients in confections.

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3.1 Properties of Water Important in Confections

In most confectionery manufacturing facilities, the source of water is the local municipality, although some plants might have their own supply (a well, for example). The quality of the water supply, and the source, can have a significant impact on the characteristics of the confections made. Of the properties that can affect candy manufacture, the presence of dissolved minerals (hardness) and metals are probably the most important. Fortunately, if any effects are observed due to these impurities in water, they are usually (bot not always) small or insignificant.

3.1.1 Water Hardness: Dissolved Minerals

As water percolates through soil and rock during its journey into the underground aquifers, it dissolves minerals depending on the nature of the earth through which it passes. Since earth's composition varies widely, water hardness can vary quite widely from region to region.

There are actually two categories of water hardness – permanent and temporary. Temporary hardness, based on calcium and magnesium bicarbonate composition, is the type that is problematic. These minerals have an inverse solubility curve, meaning they become less soluble as temperature increases (which is reverse of sucrose solubility; see Chapter 2). This causes problems when hard water is heated since the minerals precipitate as carbonates to leave a scale on the cooking surface. Permanent hardness, based on minerals such as magnesium sulfate, magnesium chloride, and calcium chloride, is less of a concern since they do not precipitate out, although they still contribute to the ionic strength of the water.

Most municipal water sources do not address hardness (usually left to water softeners in homes and businesses). Even if a water softener is used, there is still most likely substantial dissolved minerals remaining in the water. Most water softeners, particularly home softener systems, simply replace the calcium involved with temporary hardness for sodium, in a base-exchange process. Numerous salt ions are still present even in softened water unless a complete ion exchange (anionic and cationic ion removal) is conducted.

Thus, the water supply in a confectionery facility may contain high levels of dissolved minerals that may influence either the process or the product. For example, dissolved minerals can affect gelation of the stabilizers used in gummy and jelly confections (see Chapter 12). Since ionic strength is known to influence gelation of proteins and other hydrocolloids, the dissolved minerals in hard water could potentially influence their setting properties and change product quality. In general, areas where water is extremely hard would be best suited by softening the water for addition into confectionery formulations.

Dissolved minerals may also influence the action of cream of tartar on sucrose hydrolysis through its natural buffering system. In this case, production of candies where invert sugar is generated by addition of cream of tartar to the batch, as in some grained mints, may be influenced slightly by water hardness. A further problem with hard water is the reduced detergent action during cleaning. Again, to ensure consistent product, water hardness should be consistently controlled.

3.1.2 Metals

Dissolved metals (Fe, Cu, etc.) in the water supply can act as catalysts for enzyme reactions, particularly inversion of sucrose and lipid oxidation in certain confections. Fortunately, metal levels in municipal water are generally low enough that very little, if any, effect on sugar inversion has been noted. Elevated levels of lead in process water used in confections may be a concern in certain areas, especially due to the consumption of confections in children.

3.1.3 pH

Municipal water is generally neutral to slightly acidic (pH from 6.2 to 6.8); however, municipalities allow pH of up to 8.5. Such basic conditions can influence chemical reactions (e.g., Maillard browning) and color in confections through interaction with flavors. Balancing pH may be needed to ensure the desired characteristics of finished products.

3.1.4 Microbial Content

Most water supplies are not completely sterile, but all should be potable, not containing any harmful microorganisms. Microbial contamination in confections, whether through the water supply or any other source, is generally not a concern, primarily because most candies are cooked to sufficiently high temperatures to destroy most, if not all, microorganisms. The low water contents (and water activity) also provide protection against microbial problems.

3.2 Water Content in Confections

The water content in confections varies from less than 1% in chocolate and rock candy to perhaps 25–30% in some syrup candies (Table 3.1). Most types of confections have a fairly narrow range of moisture content over which that candy category is defined, although some can span quite a wide range of moisture content. Caramel, for example, can be found with moisture content as low as a few percent, in the normal range for hard candy, or as high as perhaps 18%, in soft and syrupy caramels. In general, as moisture content decreases, the texture of the confection becomes harder.

3.2.1 Cook Temperature and Water Content

As discussed in Section 2.7, the boiling temperature of a sugar solution depends on the sugar concentration according to the equilibrium boiling point relationship. Confectioners use this relationship between boiling temperature and water content to decide what cook temperature is needed to produce a candy with the desired water content. It is much easier to measure temperature under conditions of sugar boiling than it is to measure water content, particularly at very low moisture content. As long as the equilibrium relationship for a given sugar syrup is known, water content can be estimated pretty closely by simply following cook temperature. In fact, the candy thermometer was developed to help candy makers understand this correlation, although it is based on the physical properties of sugar syrups cooked to each temperature. To understand the information contained on a candy thermometer, the relationship between water content and sugar syrup viscosity (see Section 2.2) must also be understood.

Details of the state of sugar syrup based on the candy thermometer are shown in Table 3.2, along

Table 3.1 Typical water contents and water activities of confections

Category	Crystallinity[a] (%)	Moisture (%)	Water activity
Hard candy	0–2	2–5	0.25–0.40
Caramel, fudge, toffee	0–30	6–18	0.45–0.60
Chewy candies	0–10	6–10	0.45–0.55
Nougat	0–20	5–10	0.40–0.65
Marshmallow	0–20	12–20	0.60–0.75
Gummies and jellies	0	8–22	0.50–0.75
Fondants and creams	35–55	10–18	0.65–0.80
Chewing gum	30–40	3–6	0.40–0.65
Soft panned coating	60–75	3–6	0.40–0.65
Hard panned coating	80–95	0–1	0.40–0.75
Tablets and lozenges	75–95	0–1	0.40–0.75

Adapted from Ergun et al. (2010)

[a] Estimated mass of crystals within the confection

Table 3.2 Candy thermometer classifications correlated to approximate water content. Descriptions refer to state of sugar syrups cooled quickly by dropping into cold water

Boiling temperature	Water content (%)[a]	Description
106–112 °C (223–234 °F)	17.5–27.5	*Thread*: forms fine, thin threads that quickly dissipate into cold water
112–116 °C (234–240 °F)	14–17.5	*Soft-ball*: forms a soft ball that does not hold its shape
118–120 °C (244–248 °F)	11–12.5	*Firm-ball*: forms a ball that is firm enough to hold its shape, but is sticky and easily deformed
121–130 °C (250–266 °F)	7.5–11	*Hard-ball*: forms a ball that is hard and holds its shape, yet is still slightly pliable
132–143 °C (270–290 °F)	4–7	*Soft-crack*: forms hard, but not brittle threads that can be stretched between fingers
149–154 °C (300–310 °F)	2–3	*Hard-crack*: forms brittle threads that snap when bent between fingers

[a] Based on boiling point elevation for pure sucrose (Norrish 1967).

with approximate water contents for each temperature range. As expected, higher cook temperature not only leads to lower water content but also to increasingly hard sugar products as the water content decreases. At the lowest cook temperatures, water content is highest and the candy syrups have sufficiently low viscosity to be fluid-like. As cook temperature increases, water content decreases and viscosity increases, resulting in thicker and thicker candy syrups. When water content reaches the hard crack state, with only a few percent water, the candy mass is so viscous that it turns into a glass (see Section 2.9) when cooled to room temperature.

3.2.2 Measuring Water Content

Water content of sugar syrups during processing and finished products may be measured by using any of several techniques (Isengard 1995; Mathlouthi 2001; Bradley 2003; Ergun et al. 2010). These methods may be categorized generally as (1) measurement of solids content, (2) loss on drying, (3) chemical titration or (4) infrared (IR) spectroscopy analysis.

3.2.2.1 Measurement of Solids Content

Water content of sugar syrups during processing can be measured by difference if dissolved solids content can be accurately measured. The usual way to measure solids content of confectionery sugar syrups is by refractive index. Section 2.5 covers details of refractive index measurement for confectionery syrups and precautions about using the refractometer for measurement of water content. This method only works on sugar syrups up to about 90% solids content (10% moisture).

3.2.2.2 Loss on Drying

Perhaps the simplest method of measuring water content is in a drying oven. The sample is heated gently to remove water and water content is calculated from the loss of weight. Temperatures must be high enough to promote rapid diffusion of water through and out of the sample, but temperature must still be low enough to avoid boiling, crust formation, or degradation and decomposition of the sugars.

Accuracy of oven drying methods is dependent on ensuring that all the water has been removed without causing undue changes in the sample. Proper sample preparation (e.g., grinding) may be necessary to ensure that water can easily diffuse out of the candy. The loss of volatiles other than water (flavors, alcohol, etc.) present in the candy during drying also introduces errors into the measurement. Artificially high water content readings can be caused by loss of volatiles and flavors.

Another important limitation of oven drying methods is the time needed to ensure complete drying. Twenty four hours (or longer) may be needed to ensure complete water removal. In commercial operations, speed of measurement is a higher priority than accuracy, so methods of enhancing oven drying have been developed. Vacuum operation, microwave, infrared or halogen-assisted drying methods have been developed to promote more rapid drying (Ergun et al. 2010).

3.2.2.3 Karl Fischer Titration

Probably the most common method of measuring moisture content in confections is chemical titration, or the Karl Fischer titration method. This method utilizes a two-step reaction based on the iodine/iodide redox equilibrium to quantify water content (Ergun et al. 2010). The candy sample is dispersed or dissolved into an appropriate solvent (e.g., dry formamide and methanol) to free the water, and then titrated to an end-point based on the reaction between iodine and water. When all the water has been titrated, the excess iodine causes a sharp increase in potential across two electrodes. This end-point allows determination of the amount of water present based on the amount of iodine used.

Accuracy of Karl Fischer titration for water content is generally quite good in the range of water content found in most confections, except perhaps for hard candies with a very low water content (<1–2%). Probably the most critical aspect of Karl Fischer titration for confections is adequate dispersion of the sample to expose water within the interior of the candy. Proper sample preparation and choice of dispersion solvent is critical to accurate water content measurement with this method. For example, grinding of a hygroscopic candy product (e.g., hard candy) in a humid environment will lead to unexpectedly high water content readings since the ground candy powder will quickly pick up moisture from the air. In extreme cases, sample preparation may need to be done in a controlled humidity environment.

3.2.2.4 Infrared (IR) Spectroscopy

Recently, measurement of water content by near infrared (NIR) analysis has become more common (Mathlouthi 2001). Electromagnetic radiation in the near infrared region of the spectrum is applied to the food and the absorption spectra observed. Since water absorbs strongly in the IR region, there is a characteristic water absorption spectrum that can be used to quantify water content after a standard curve has been generated from other methods (e.g., Karl Fischer titration). Typically, water content measurement is based on signals at 1,400–1,450 and 1,920–1,950 nm, which indicate the different vibrational modes of water molecules (Isengard 2001).

Although NIR measurement of water content is quite rapid, care must be taken to ensure that the true water content of a sample is measured. Numerous factors (i.e., color, particle size, thickness, texture, etc.) can influence NIR measurement, so sample preparation is critical to accurate and reproducible results. The interior of the candy sample must be exposed to avoid measuring only surface moisture content.

3.3 Water Activity and Equilibrium Relative Humidity (ERH)

Water activity is a well-known concept in the food industry. As an indicator of water's ability to interact chemically, it is often used to describe the availability of water to participate in various reactions, including microbial growth. Thermodynamically, water activity is defined as the ratio of the fugacity (or the tendency to escape) of water molecules in the product to that in a reference system. Since fugacity is rarely used (difficult to measure), water activity may be approximated as the ratio of activity coefficients of water in the product to that same reference state (usually pure water). Activity coefficients also are rarely used (also difficult to measure) in the food industry; thus, water activity is often defined as the ratio of partial pressures of water over the food product to that over pure water. The form of water activity, a_w, most commonly used in the food industry is

$$a_w = p_w^f / p_w^o = RVP \tag{3.1}$$

where, p_w^f is water vapor pressure above the food and p_w^o is vapor pressure of pure water at the same temperature. Because a_w defined in Equation 3.1 is not true thermodynamic water activity, the parameter, RVP, or relative vapor pressure, is sometimes quoted.

Water activity of pure water is one. This is the reference state to which all food products are compared. In pure water, individual water molecules interact and form clusters through hydrogen bonding. The polar nature of water, where one end of the molecule has a slight negative charge and the other has a slight positive charge (even though the molecule as a whole is neutral), is what leads to these molecular interactions in pure water. However, hydrogen bonding energies are quite small and the molecules are easily broken apart by normal vibrational energy at room temperature. Thus, water clusters form and dissociate very quickly. For water in contact with air, there is also a release of molecules from the surface into the air. This is normal evaporation, the rate of which is primarily dependent on temperature, with faster water evaporation at higher temperatures. At any temperature, air can only hold a certain amount of water vapor. The equilibrium water vapor pressure, p, of moisture in air at any temperature, T, can be found in Table 3.3. Alternatively, it can be calculated from the Antoine equation.

$$\log(p) = A - \frac{B}{C+T} \tag{3.2}$$

Here, p is given in mm Hg, T in °C, and the constants A, B and C are 8.07131, 1,730.63 and 233.426, respectively.

The addition of solute molecules, like sugars, starches, proteins and salts, to water causes interactions between the solutes and the water molecules. For example, a single sucrose molecule in water has a hydration shell containing five water molecules due to hydrogen bonding between the polar water molecules and the polar sites (hydroxyl groups) on the sucrose molecule (Mathlouthi 1995). Again, hydrogen bonding energies are quite small and are easily disrupted by normal vibrational energy at room temperature. Thus, when a water molecule associates with sucrose at a hydrogen bonding site, it does so only for a very short time. It is then released back into the bulk water and another water molecule arrives to take its place on the sucrose hydrogen bonding site. In this way, there are continuously, on average, five water molecules associated with the sucrose molecules, but they are always changing.

Table 3.3 Water vapor pressure at different temperatures

Temperature (°C)	Vapor pressure (kPa)
0	0.6
10	1.2
20	2.3
30	4.2
40	7.4
50	12.3
60	19.9
70	31.2
80	47.3
90	70.1
100	101.3

As solute molecules are added to solution, the number of water molecules decreases and the number of interactions between solute and water increases dramatically. Fewer water molecules can escape from the surface into the air so that the vapor pressure of water over a concentrated sugar solution is less than the vapor pressure of moisture over pure water. The water activity, the ratio of these two vapor pressures, decreases below one due to the presence of the solute.

Water activity is related to water content, but the nature of the solutes is also important since different solutes affect water in different ways. Table 3.1 shows the typical range of water activity in different confectionery categories. Water activity varies from as low as about 0.25 for hard candy to as high as about 0.8 for candies with high water contents.

Recently, the concept of water activity has been the subject of much discussion as the limitations of Equation 3.1 become more apparent. Several simplifications and assumptions were made to go from true thermodynamic water activity (ratio of fugacities) to the ratio of vapor pressures used in Equation 3.1. Besides the assumption that the ratio of partial pressures is equal to the ratio of fugacities (only true when activity coefficients in the two states are identical), there is an assumption of equilibration. That is, it is assumed that there is sufficient time for the water molecules in the food to equilibrate with the water molecules in the air surrounding the food (and where we measure vapor pressure). When water activities are very high, the assumption of equilibrium is probably true and the measured ratio of vapor pressures is close to the actual water activity. However, in other cases, most notably when water content is very low, the assumption of equilibration is likely to be incorrect and the measured relative vapor pressure may be different from true water activity. Recently, terms like relative vapor pressure and even food relative humidity have been suggested to replace the term water activity. Despite these limitations, however, the concept of water activity is still widely used.

During storage, candies may either pick up moisture from the air (absorption) or lose moisture to the air (drying or desorption). Thermodynamically, it is the difference in chemical potentials between water in the air and water in the candy that drives the transfer of water. From a practical standpoint, the difference in relative humidity of the air and the water activity of the food is what drives absorption or desorption, with a greater difference driving more and faster moisture migration.

The relative humidity at which the candy neither picks up moisture nor dries out is called the equilibrium relative humidity (ERH). At the ERH, water in the air and water in the candy are in equilibrium, meaning there is no net exchange of water molecules between air and food. Note that equilibrium between water molecules in the air and candy means that the net exchange of water molecules in each direction is equal. The same number of molecules migrate from air to candy as migrate from candy to air. This continuous exchange can still lead to modifications in properties.

In general, ERH is simply the water activity multiplied by 100 to give a value in percent.

$$ERH(\%) = 100 \cdot a_w \tag{3.3}$$

For example, a caramel with water activity of 0.6 (Table 3.1) has an ERH of 60%. When exposed to air with relative humidity less than 60%, that caramel will lose moisture to the air, undergoing physical and chemical changes (e.g., firming, hardening) that often lead to the end of shelf life. In turn, if held in air with RH greater than 60%, that caramel will pick up moisture from the air, causing potential problems including stickiness and softening. Although packaging can slow down this exchange of moisture, the caramel will slowly change during storage as it loses or gains moisture with the air. Moisture migration is covered in greater depth in Section 3.5.

3.3.1 Measurement of Water Activity

With recent advances in sensor designs, measurement of water activity is now quite simple and straightforward (Ergun et al. 2010). However, problems with sample preparation and equilibration time between candy and air may still cause erroneous readings.

3.3.1.1 Hygrometry

The traditional method of measuring water activity used the hair hygrometer, which is based on the sensitivity of a hair to humidity. As the water content of the hair changes due to exposure to humid or dry air (due to moisture sorption or loss of the keratinaceous protein of the hair), the length of the hair changes. The water in a candy placed into a closed environment equilibrates with the air at the ERH, the value of which can be read from the length of the hair. The main problem with hair hygrometers is lack of accuracy.

Hygrometers may also be based on the change in conductivity or resistance of a hygroscopic salt to changes in relative humidity. The candy is placed in an environment with the hygroscopic salt and changes in the electrical conductivity of the salt is measured by potentiometer and correlated to ERH (and thence, to a_w). Electric hygrometers are accurate and simple to use, but suffer from potential contamination when organic volatiles escape from the candies.

3.3.1.2 Dew Point Methods

Modern water activity measurements are generally based on the dew point principle. Air in equilibrium with the food is passed across a cooled mirror or sight glass and the temperature at which condensation first occurs is measured. Relative humidity can then be obtained from the psychrometric chart (a thrmodynamic chart that, among other things, relates humidity with wet bulb, dry bulb and dew point temperatures). Assuming equilibration of water between the air and the food sample, this relative humidity is then converted into water activity. Dew point measurements are suitable across the entire range of a_w and are relatively quick (1–2 h) (von Elbe 1986; Ergun et al. 2010).

For accurate measurement of water activity of confections, the sample is often ground to allow moisture from within the candy piece to be exposed to the air in the meter. However, great care must be taken during sample preparation so that moisture uptake or loss to room air during sample preparation does not occur. In extreme cases, a humidity controlled sampling environment may be needed to ensure accurate water activity measurement of confections. Further, calibration of the unit should be checked periodically by comparing actual readings of a_w standards available from the manufacturer.

One limitation of the dew point method is that the presence of alcohol in the candy can cause significant errors.

3.3.2 Prediction of Water Activity

Due to earlier difficulties in measurement methods, researchers developed methods to predict water activity based on product composition. It is primarily the sweeteners in confections that affect water activity, so empirical equations based on sweetener type and concentration were developed to predict water activity based on composition. In the later 1940s and early 1950s, Grover (1947) and Money and Born (1951) developed empirical equations that correlated water activity with composition of various sugar solutions. These equations worked reasonably well for predicting water activity for systems with sugar concentrations less than 80–90%.

In the 1960s, Norrish (1966) developed a semi-empirical model based on thermodynamic principles for calculating water activity for sugar solutions and verified his results experimentally for a wide range of important confectionery syrups. The Norrish equation for calculating the relative vapor pressure (RVP) of a sucrose solution is:

$$\log(RVP) = \log(x_1) - K_{12}x_2^2 \qquad (3.4)$$

where, x_1 is the mole fraction of water, x_2 is the mole fraction of sucrose, and K_{12} is molecular interaction factor specific for the sugar in solution. For sucrose solutions, Norrish provided a value of $K_{12} = -2.60$. For mixtures of sugars commonly found in confectionery syrups, Equation 3.4 is modified to Equation 3.5 to account for multiple contributions of each sugar present.

$$\log(RVP) = \log(x_w) - \sum[(-K_i)^{0.5} x\ ]^2 \quad (3.5)$$

Here, x_w is the mole fraction of water, x_i is the mole fraction of each of the sugars in the mixture, and K_i are the individual factors for each of the sugars.

Chirife et al. (1980) refined the Norrish method and provided K_i values that predict water activity more accurately for sugar and polyol systems. Table 3.4 provides K values that can be used in Equation 3.5 to predict water activity of sugar mixtures to a reasonable degree of accuracy.

The effects of glucose syrups on water activity are taken into account through their average molecular weight (MW) based on the dextrose

Table 3.4 Values of Norrish constant, K, as given by Chirife et al. (1980)

Ingredient	K[a]
Sucrose	2.81
Maltose	1.97
Glucose	0.98
Xylose	0.67
Sorbitol	0.72
Erythitol	0.58
Glycerol	0.50
Mannitol	0.39

From Ergun et al. (2010)

[a] Note that Chirife et al. (1980) provide K values in terms of a natural log expression, rather than the $\log_{10}$ expression of Norrish (1966). K values here are converted to the Norrish form

equivalent (DE). Bussiere and Serpollini (1985) provided equations for estimating K values for glucose syrups.

$$MW = 552 - 3.64(DE) \tag{3.6}$$

$$K = 0.02(DE) - 3.28 \tag{3.7}$$

These K values would be used as appropriate in Equation 3.5 to determine the contribution of glucose syrups on water activity.

Recent developments in predicting water activity were reviewed by Sereno et al. (2001). Advances in group contribution methods, which account for thermodynamic interactions among the different chemical groups of the molecular species under consideration, have greatly enhanced our ability to predict thermodynamic properties like water activity (and boiling point elevation). However, these numerical approaches are beyond the scope of this book.

3.3.3 Water Activity and Microbial Stability

Table 3.5 gives the range of water activities over which certain types of microorganisms can grow. Typically, if water activity is less than 0.86, the product is generally considered to be safe to pathogenic bacterial growth. However, numerous microorganisms can still grow (and thrive) at water activities significantly lower than 0.86. To be sure that no osmophilic molds can grow on a candy, the water activity should be below about 0.65.

In general, most confections are relatively stable to microbial growth, with water activities less than 0.6 (Table 3.1). Exceptions to this are syrup candies, ganache, and some types of fondant, caramel and fudge. If these products are formulated incorrectly, with insufficient dissolved sugars to reduce water activity enough, they can support mold growth. For example, fondants should be formulated with sufficient corn syrup or invert sugar to reduce water activity of the liquid phase below the level of concern for microbial growth. Fudge with mold spots, although not common, occurs often enough to be a concern, as it does in ganache, especially those with raw spices added. The candy maker may choose to add preservatives (e.g., potassium sorbate) to maintain the desired soft texture that comes with higher a_w, although proper formulation to reduce a_w can give extended shelf life without concerns for mold growth.

Table 3.5 Growth of microorganisms dependent on water activity

Water activity range	Microorganisms	Confections
>0.86	Normal bacteria and pathogens, many yeasts	Ganache, very soft fondant
0.80–0.86	Normal molds, some yeasts	Soft fondant, soft jellies, etc.
0.70–0.80	Molds, yeasts	Fondant, fudge, jellies, grained nougats, marshmallow, etc.
0.60–0.70	Osmophilic yeasts, some molds	Fudge, fondant, hard jellies, nougat, soft caramel, etc.
<0.60	None	Caramel, toffee, jellies, gum, hard candy, chocolate, etc.

From Ergun et al. (2010)

3.4 Moisture Absorption or Desorption Profiles

Candies that are exposed to air with relative humidity different from the ERH will either pick up moisture from that air or dry out as the moisture in the candy and the air attempt to equilibrate. This exchange of moisture generally is not good for candy quality as the gain or loss of moisture, particularly at the surface exposed to the air, often causes unacceptable changes in texture (stickiness, hardening, etc.) or other quality attributes (color, crystallization, flavor loss, etc.). For example, hard candy exposed to air with relative humidity greater than about 30% quickly picks up moisture from the air and the surface either becomes sticky or it grains, depending on sugar composition (ratio of sucrose to glucose syrup). Either of these events would be considered as the end of shelf life. Thus, any change in moisture under unfavorable storage conditions is of considerable importance to confectioners.

Sorption profiles are found by measuring the moisture content of a candy after it has been allowed to equilibrate with air of a certain relative humidity. The resulting curve, relating water content and water activity (or relative vapor pressures) provides an indication of the hygroscopicity (or capability to pick up moisture from air) of a material. Some typical sorption curves are shown in Figure 3.1.

Many confections follow Type II or III sorption isotherms. These include caramel, fudge and nougat as well as jelly and gummy candies. Hard candies and cotton candy typically are very hygroscopic and are likely to follow Type I profiles. More lower molecular weight sugars (as might happen if excessive inversion has occurred during cooking) generally leads to more hygroscopic behavior. Some sugar-free candies based on sorbitol and isomalt have been shown to exhibit Type III behavior (Hadjikinova et al. 2003). Note that crystalline materials are typically not hygroscopic, as seen in Figure 3.1 for the crystalline sucrose sorption isotherm. Due to the tight bonding of the crystal lattice, water molecules can only interact at the surface of a crystal. Only when a sufficiently large number of water molecules have adsorbed onto the crystal surface does dissolution occur (called the deliquescent point).

3.4.1 Measuring Absorption or Desorption Curves

Sorption or desorption curves are typically generated by holding the candy in air containing different relative humidities and measuring the water content after equilibration. This may be done in a variety of ways.

Probably the oldest method of measuring of moisture sorption curves is to hold the candy in a controlled environment (e.g., a dessicator) where the relative humidity can be accurately controlled. Saturated salt solutions are often used to control relative humidity. Table A.3.1, in the appendix, shows the relative humidities of air in equilibrium with saturated salt solutions (Bell and Labuza 2000). The candy must be held at this relative humidity for sufficient time to allow equilibration of the moisture between the candy and the air. When equilibrium is attained, the moisture content of the candy is measured (see previous section) to obtain one point on the sorption/desorption curve. A bank of controlled relative humidity chambers, each with a different saturated salt solution, is needed to obtain a complete understanding of the sorption/desorption behavior of a candy.

More recently, analytical equipment is available that can quickly and easily measure the entire span of the sorption/desorption curve.

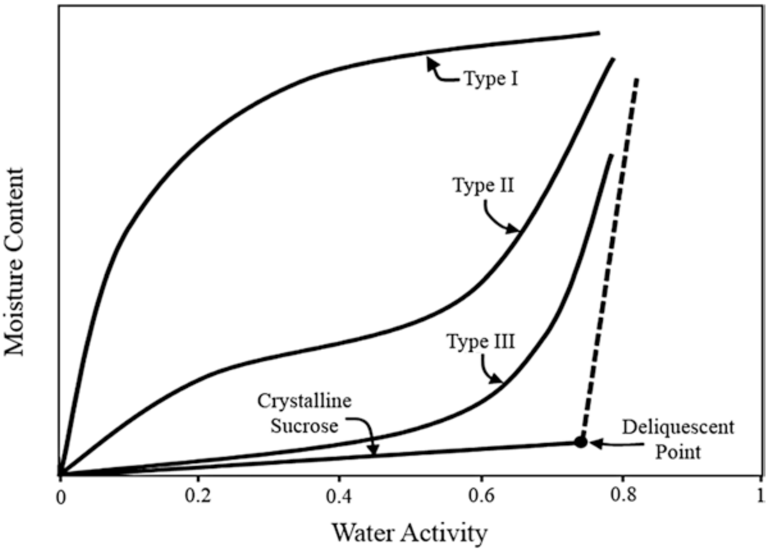

Figure 3.1 Common moisture sorption isotherms

These automated "controlled atmosphere microbalances" allow rapid measurement of sorption and desorption curves.

3.4.2 Temperature Effects

Since the amount of water vapor that air can hold varies with temperature (Table 3.3), ERH is a function of temperature. When temperature goes up, air can hold more moisture (see Section 2.7), which means that water from the candy tends to migrate into the air (drying out). The rate that a candy dries out depends on how much the temperature goes up, but also on how fast water diffuses through the candy matrix and into the air. Typically, diffusivity of water in a candy is directly related to the water content, with higher diffusivity found with higher water content, although the structural aspects of the candy also influence diffusion rates. Thus, the amount of moisture lost from candy to air when temperature goes up depends on the temperature extreme and the time scale over which the temperature fluctuates. The loss of moisture typically causes the candy to become unacceptably hard, a natural result of drying out.

When temperature goes down again, the air can hold less moisture and the now excess water vapor in the air tries to go back into the candy. However, the time it takes for moisture at the surface of a candy to diffuse back into a complex candy structure is generally quite long and moisture may pool at the surface, forming pockets of relatively dilute sugar syrup. This can have several negative consequences, including mold growth and unsightly color blemishes.

3.5 Moisture Migration and Shelf Life

Understanding and managing water movement is important to controlling shelf life of many confections. In many candies, it is a change in moisture during storage that leads to end of shelf life.

3.5.1 Moisture Migration

When candy is exposed to air with a relative humidity different from the ERH, moisture gain or loss occurs as the system drives towards a new moisture equilibrium. Furthermore, when the different layers of a multi-layered candy have different water activity, moisture migration occurs between the layers until they equilibrate at a common water activity, as shown schematically in Figure 3.2 for a chocolate-covered multi-domain candy bar. Both sources of water migration generally lead to undesirable changes in product quality (texture, flavor, aroma, appearance, etc.) and eventually signal the end of shelf life.

The rate at which moisture migration occurs in a confection is dependent on several parameters: the initial difference in water activities, the mechanisms of moisture transport within the system, and the presence of any moisture barriers. The driving force for moisture migration is a difference in water activity (or more accurately, a difference in chemical potential), not a difference in water content. That is, two layers of a candy bar may have different water content, but as long as they have the same water activity, no net moisture change will occur between the layers.

As with all rate processes, the magnitude of the driving force (difference in water activities) plays an important role in the rate of moisture migration. For example, a candy with water activity of 0.5 (ERH of 50%) held in a dry environment (relative humidity of 10%) loses moisture much faster than if it is stored in air at a relative humidity of 40%. The difference between the ERH of the candy is greater when the air is drier. In the same way, two domains of a candy bar (i.e., cookie and caramel, or caramel and nougat) will transfer water at a rapid rate if the difference in their initial water activities is high. For example, the difference in water activities of cookie and caramel are greater than that between caramel and nougat, so the caramel-cookie candy bar will undergo moisture migration more quickly than the caramel-nougat candy bar. However, over time, as the water activities of the

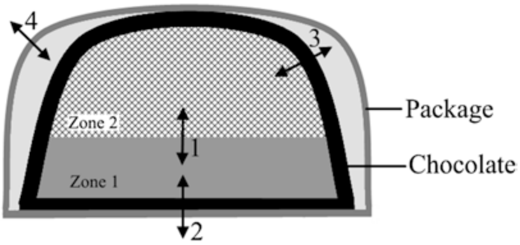

Figure 3.2 Moisture migration pathways for chocolate-covered candy bar system. *1* Migration between interior zones; *2* migration between interior zones and outside air (directly through chocolate and package layer in direct contact); *3* migration between interior zones and headspace; *4* migration between headspace and outside air

two components gets closer, the rate of moisture migration decreases due to the lower driving force. To minimize moisture transport, differences in water activity between the elements of a confection and its package (Figure 3.2) should be minimized.

The rate at which moisture migration occurs is also dependent on how quickly water moves through and between each of the elements. Water migrates within a candy primarily by liquid diffusion, although capillary forces and thermal or pressure gradients may also impact rate of migration. Diffusion rates depend on temperature, water content, and the porosity and structural nature of the matrix through which the water is diffusing.

In general, diffusion rates and viscosity of a homogeneous matrix are inversely related. Thus, factors that decrease viscosity increase diffusion rates. That is, diffusion rate increases as temperature goes up (and vice versa). For this reason, storage of candy at elevated temperatures generally leads to the most rapid rate of moisture migration and loss of shelf life. Viscosity also increases as water content goes down, so diffusion of water is slower in candies with lower moisture content. That is, water diffusion in sugar syrup candies (20–25% moisture) is orders of magnitude faster than diffusion in chewy candies (8–10% moisture). Diffusion rates are even lower in hard candies (3–4% moisture), where molecular mobility is severely limited by the high viscosity in the glassy state. Moisture migration through a glassy sugar matrix is extremely slow, although what limited moisture mobility still exists can ultimately lead to the end of shelf life of hard candies over an extended time.

The nature of the candy matrix also affects moisture migration rates. Structural elements, including physical cracks and crevices, emulsion droplets, protein aggregates, and gelled structures, affect the ability of water molecules to diffuse from one point to another over time. In gummy and jelly candies, for example, moisture diffusion within each gel matrix element is quite rapid, but migration between neighboring elements is much slower since the protein or polysaccharide gelling agent forms an effective barrier. Protein aggregates in caramels, emulsion droplets (chews, caramel, etc.), and air cells (nougat, marshmallow, etc.) in various candies also affect moisture migration although not nearly as effectively as gelled structures. Physical cracks and crevices, on the other hand, speed moisture migration from one point to another by providing a conduit for water to move.

To prevent moisture from moving between elements of a confection, water barriers may be used. Packaging materials provide such a barrier for moisture migration with the surrounding air. Various plastics and metal foil packages are used for confections, each with their own inherent water permeability. Candies that are prone to either picking up or losing moisture should be packaged in materials with the lowest water permeability to provide extended shelf life. However, even when the best water barrier is used for packaging, sealing of the edges of the package is also critical. Poor packaging (i.e., twist-wrapped hard candy) and improperly sealed packages provide direct transport of water vapor molecules into or out of the candy package.

In multi-domain confections, as seen in Figure 3.2, water barriers may be used between the different domains to reduce moisture migration. The domain with higher water activity loses moisture to the domain with lower water activity, with water continuing to migrate until the water activities of the two domains have equilibrated. The end of shelf is signaled by the time it takes for sufficient moisture to migrate such that the texture or flavor of one of the elements is no longer acceptable. To extend shelf life, an edible water barrier can be introduced between the two domains. Typically, fat-based barriers are used to inhibit moisture migration and extend shelf life, although some protein or cellulose-based films may provide enough barrier properties to sufficiently extend shelf life. Edible moisture barriers should not detract from the taste or texture of the candy, and to be effective, should be easy and efficient to apply, providing complete coverage of the two domains without holes or cracks. Because of these problems associated with edible films, their use in confections has not yet found widespread application.

3.5.2 Shelf Life

Moisture migration often causes the end of shelf life for many confections. Changes in moisture content, whether moisture gain or loss, can cause significant changes in product quality. The chapters on each candy category provide detail of changes that occur in shelf life, so only a brief review of the main mechanisms for end of shelf life related to moisture is given here. A recent example case study for calculating the end of shelf life of a high moisture confection (marshmallow) due to moisture loss through a packaging layer can be found in Hartel et al. (2013).

3.5.2.1 Changes Associated with Moisture Migration

Water content in candy often governs texture and when water content changes during storage, textural changes also occur. For example, a caramel or marshmallow exposed to air of low relative humidity quickly dries out and becomes hard. Furthermore, moisture migration in a multi-layer candy bar may occur between each of the different layers in contact. The loss of water from one domain causes it to become harder, while the gain in moisture of the other domain may cause it to become soft and soggy.

Some confections may pick up sufficient moisture from the surrounding air that they become sticky. Hard candy exposed to air of relative humidity picks up moisture from the air and forms a sticky syrup layer at the surface. Without proper packaging, stickiness of hard candies can occur within days at elevated humidity and temperature.

In some cases, moisture sorption may lead to graining or recrystallization of sugars during storage. Candies that do not have high concentrations of crystallization inhibitors (corn syrup, invert sugar, etc.) are prone to graining if sufficient moisture is adsorbed. For example, cotton candy as well as hard candies with relatively low (30%) corn syrup content are prone to graining when exposed to humid air.

In hard candies, flavor molecules embedded within the glassy matrix are held there by the limited diffusion rate in the glassy state. However, when moisture sorption causes a decrease in glass transition temperature, there is a significant increase in molecular mobility. Flavor diffuses out of the candy, eventually leading to end of shelf life. When the matrix grains, or recrystallizes, the flavor molecules are concentrated within the remaining liquid matrix (between the crystals), thereby increasing the driving force for flavor loss.

The physical changes that occur due to moisture uptake or loss can also lead to changes in appearance of candies. A continual problem with hard-panned candies is development of mottled colors due to moisture migration. If insufficient water is dried from individual hard-panned sugar-coated layers, water soluble dyes are prone to moving as the moisture moves to equilibrate within the sugar shell over time. The result is a mottled appearance.

Appendix

Table A.3.1 Water activity of saturated salt solution from 10 to 40 °C

°C	Water activity			
	Cesium fluoride	**Lithium bromide**	**Zinc bromide**	**Potassium hydroxide**
10	0.049 ± 0.016	0.071 ± 0.007	0.085 ± 0.007	0.123 ± 0.014
15	0.043 ± 0.014	0.069 ± 0.006	0.082 ± 0.006	0107 ± 0.011
20	0.038 ± 0.011	0.066 ± 0.006	0.079 ± 0.005	0.093 ± 0.009
25	0.034 ± 0.009	0.064 ± 0.005	0.078 ± 0.004	0.082 ± 0.007
30	0.030 ± 0.008	0.062 ± 0.005	0.076 ± 0.003	0.074 ± 0.006
35	0.027 ± 0.006	0.060 ± 0.004	0.075 ± 0.003	0.067 ± 0.004
40	0.024 ± 0.005	0.058 ± 0.004	0.075 ± 0.002	0.063 ± 0.004
	Sodium hydroxide	**Lithium chloride**	**Calcium bromide**	**Lithium iodide**
10		0.113 ± 0.004	0.216 ± 0.005	0.206 ± 0.003
15	0.096 ± 0.028	0.113 ± 0.004	0.202 ± 0.005	0.196 ± 0.002
20	0.089 ± 0.024	0.113 ± 0.003	0.185 ± 0.005	0.186 ± 0.002
25	0.082 ± 0.021	0.113 ± 0.003	0.165 ± 0.002	0.176 ± 0.001
30	0.076 ± 0.017	0.113 ± 0.002		0.166 ± 0.001
35	0.069 ± 0.015	0.113 ± 0.002		0.156 ± 0.001
40	0.062 ± 0.012	0.112 ± 0.002		0.146 ± 0.001
	Potassium acetate	**Potassium fluoride**	**Magnesium chloride**	**Sodium iodide**
10	0.234 ± 0.005		0.335 ± 0.002	0.418 ± 0.008
15	0.234 ± 0.003		0.333 ± 0.002	0.409 ± 0.007
20	0.231 ± 0.003		0.331 ± 0.002	0.397 ± 0.006
25	0.225 ± 0.003	0.308 ± 0.013	0.328 ± 0.002	0.382 ± 0.005
30	0.216 ± 0.005	0.273 ± 0.011	0.324 ± 0.001	0.362 ± 0.004
35		0.246 ± 0.009	0.321 ± 0.001	0.347 ± 0.004
40		0.227 ± 0.008	0.316 ± 0.001	0.329 ± 0.004
	Potassium carbonate	**Magnesium nitrate**	**Sodium bromide**	**Cobalt chloride**
10	0.413 ± 0.004	0.574 ± 0.003	0.622 ± 0.006	
15	0.432 ± 0.003	0.559 ± 0.003	0.607 ± 0.005	
20	0.432 ± 0.003	0.544 ± 0.002	0.591 ± 0.004	
25	0.432 ± 0.004	0.529 ± 0.002	0.576 ± 0.004	0.649 ± 0.035
30	0.432 ± 0.005	0.514 ± 0.002	0.560 ± 0.004	0.618 ± 0.028
35		0.499 ± 0.003	0.546 ± 0.004	0.586 ± 0.022
40		0.484 ± 0.004	0.532 ± 0.004	0.555 ± 0.018
	Potassium iodide	**Strontium chloride**	**Sodium nitrate**	**Sodium chloride**
10	0.721 ± 0.003	0.757 ± 0.001	0.775 ± 0.005	0.757 ± 0.002
15	0.710 ± 0.003	0.741 ± 0.001	0.765 ± 0.004	0.756 ± 0.002
20	0.699 ± 0.003	0.725 ± 0.001	0.754 ± 0.004	0.755 ± 0.001
25	0.689 ± 0.002	0.709 ± 0.001	0.743 ± 0.003	0.753 ± 0.001
30	0.679 ± 0.002	0.691 ± 0.001	0.731 ± 0.003	0.751 ± 0.001
35	0.670 ± 0.002		0.721 ± 0.003	0.749 ± 0.001
40	0.661 ± 0.002		0.710 ± 0.003	0.747 ± 0.001
	Ammonium chloride	**Potassium bromide**	**Ammonium sulfate**	**Potassium chloride**
10	0.806 ± 0.010	0.838 ± 0.002	0.821 ± 0.005	0.868 ± 0.004
15	0.799 ± 0.006	0.826 ± 0.002	0.817 ± 0.004	0.859 ± 0.003
20	0.792 ± 0.004	0.817 ± 0.002	0.813 ± 0.003	0.851 ± 0.003
25	0.786 ± 0.004	0.809 ± 0.002	0.810 ± 0.003	0.843 ± 0.003

(continued)

Table A.3.1 (continued)

°C	Water activity			
30	0.779 ± 0.006	0.803 ± 0.002	0.806 ± 0.003	0.836 ± 0.003
35		0.798 ± 0.002	0.803 ± 0.004	0.830 ± 0.003
40		0.794 ± 0.002	0.799 ± 0.005	0.823 ± 0.003
	Strontium nitrate	**Potassium nitrate**	**Potassium sulfate**	**Potassium chromate**
10	0.906 ± 0.004	0.960 ± 0.014	0.982 ± 0.008	
15	0.887 ± 0.003	0.954 ± 0.010	0.979 ± 0.006	
20	0.869 ± 0.003	0.946 ± 0.007	0.976 ± 0.005	
25	0.851 ± 0.004	0.936 ± 0.006	0.973 ± 0.005	0.979 ± 0.005
30		0.923 ± 0.006	0.970 ± 0.004	0.971 ± 0.004
35		0.908 ± 0.008	0.967 ± 0.004	0.964 ± 0.004
40		0.890 ± 0.012	0.964 ± 0.004	0.959 ± 0.004

From Bell and Labuza (2000)

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4 Fats, Oils and Emulsifiers

Abbreviations

CMC	Critical micelle concentration
DAG	Diacylglycerol, or diglyceride
DSC	Differential scanning calorimeter
FFA	Free fatty acid
HLB	Hydrophilic-lipophilic balance
MAG	Monoacylglycerol, or monoglyceride
NMR	Nuclear magnetic resonance
PGPR	Polyglycerol polyricinoleate
SFC	Solid fat content
SFI	Solid fat index
TAG	Triacylglycerol, or triglyceride

4.1 Introduction

Various definitions have been offered to define lipids, although the terms fat, oil and lipid are often used interchangeably in the food industry to denote a certain type of molecular structure. In general, lipids are molecules that contain a significant proportion of aliphatic or aromatic hydrocarbons. Lipids may also be defined as the various soft or semi-solid organic compounds comprising the glyceride esters of fatty acids and associated compounds such as hydrocarbons or substituted hydrocarbons (fatty acids, waxes, soaps, detergents, emulsifiers), acylglycerols (mono-, di- and triacylglycerols), glycerophospholipids (e.g., lecithin), sterols (e.g., cholesterol), and oil-soluble vitamins (A, D, E and K).

Typically, the difference between a fat and an oil is one of physical state at room temperature. A fat is solid (or semi-solid) at room temperature, whereas an oil is liquid. However, this general rule is not always followed since room temperature varies widely over the globe and the term fat is often used to signify lipids of any type. For example, palm oil is partially solidified at "normal" room temperature, 22 °C (72 °F), in the northern hemisphere.

Fats and oils are derived from a variety of sources, including animals (lard, tallow, etc.), ruminants (e.g., milk fat), marine animals (fish oils) and vegetable sources. Oils from microbial sources are also becoming more and more important in the food industry. Most important in confections are the vegetable fats, although milk fat (bovine) plays an important role as well. It is rare that lard or tallow or any of the marine oils are incorporated into confections.

Lipids play several important roles in confections. In some candies, the fat is in an emulsified state, dispersed through a continuous matrix usually made of sugars dissolved in water (as in caramel, fudge or toffee). In these products, the fat is present to deliver certain flavor attributes (as in milk fat in caramel or the fat in a cream hard candy), but it also impacts the texture of the final product (shortness or lubricity in the mouth as in a fruit chew product) and may also impact overall processing during manufacture. For example, the presence of fat in a chewy candy decreases the stickiness during processing as well as during

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consumption. In addition, fats (fully hydrogenated vegetable fats or emulsifiers) may be used as a lubricant in tableted candies to enhance release from the mold after compression.

In some products, such as chocolates and compound coatings, the fat is the continuous phase and governs the physical and textural properties of the final product. The snap or hardness of chocolate is controlled by the extent and nature of the crystalline lipid phase. Besides the solid fat content, controlling the proper polymorphic form as well as the dispersion of the crystalline fat in these products is necessary to obtain products with desired qualities (i.e., glossy appearance, contraction from mold, resistance to bloom, etc.).

In some candies, different fats may be present in different domains, as in multilayered products (e.g., peanut butter coated in chocolate or chocolate-covered biscuits) where migration of one fat into the other can cause significant problems in storage stability. In other cases, lipids are used to prevent moisture migration, as in, for example, a wax/lipid coating on a panned sugar candy piece. In certain systems, mixtures of fats may occur, as in milk chocolate containing milk fat and cocoa butter or compound coatings containing cocoa butter and another vegetable oil. Thus, the compatibility of the two fats is important to texture and shelf life.

To control lipids in confections, several important points must be considered. First, it is necessary to understand lipid chemistry and the reactions that take place that might signal end of shelf life. Further, since lipids form important structures in confections, understanding the phase behavior and crystallization kinetics is critical to obtaining the desired textural properties. Natural lipids often do not have the appropriate functional properties, so it is also necessary to know how to modify them to put them to the best use in confections. Finally, fats are often emulsified in confections, so understanding emulsifiers and emulsification is another key element for obtaining desirable properties with extended shelf life. If these principles are applied correctly, an enjoyable stable product can be created for the consumer.

4.2 Chemistry of Fats and Oils

The basic element of natural fats is the aliphatic chain or hydrocarbon, an organic molecule made up of carbon atoms bonded to one another (and oxygen and hydrogen molecules) in a chain.

4.2.1 Chemical Structures

The main building block of natural fats is the fatty acid, which is combined in various ways to form the primary chemical constituent of fats, the triacylglycerol (or triglyceride, TAG). Minor constituents, including free fatty acids, mono- and diglycerides, sterols and phospholipids, may only be present in small amounts, but sometimes these minor lipids may have significant effect on the chemical and physical properties of natural fats. Lipp and Anklam (1998a, b) review both the analytical methods and chemical composition of cocoa butter and other fats of importance in chocolate confectionery products.

4.2.1.1 Fatty Acids

Fatty acids are hydrocarbon molecules with a carboxylic acid at one end, as shown in Figure 4.1. Fatty acids are distinguished by the nature of the carbon chain through either chain length, degree of unsaturation or orientation of the unsaturated double bonds. Fatty acids can have different chain lengths, composed of carbon numbers from 4 to 22, or even higher. The carbon bonds in fatty

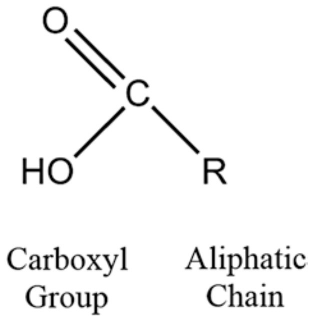


Figure 4.1 Generic structure of a fatty acid, where *R* is an aliphatic chain

acids can either be all saturated or partially unsaturated with double bonds arranged between adjacent carbon atoms. Some fatty acids may have multiple unsaturated double bonds. Furthermore, unsaturated double bonds can be organized in various forms, the most common being the *cis* and *trans* conformations. The chemical structures, along with their common names, are demonstrated in Figure 4.2 for the common fatty acids varying in size from C4:0 to C18:3.

The fatty acid composition of several natural fats is given in Table 4.1. Milk fat contains a wide range of fatty acids, with from 4 to 20 carbon atoms. Milk fat is somewhat unique among natural fats due to the fairly high content of short-chain (C4–C8) fatty acids. Vegetable fats, such as cocoa butter, palm oil and soybean oil, contain mostly long-chain fatty acids (C16 or C18), with liquid oils containing more mon- and polyunsaturated fatty acids. Vegetable fats used in the confectionery industry are often categorized based on the predominant fatty acid composition. Coconut and palm kernel oil are called lauric fats because of their high concentration of lauric acid, both of which contain nearly 50% lauric acid. Other vegetable fats contain longer-chain fatty acids and, in the confectionery industry, are called nonlauric fats.

4.2.1.2 Glycerides

Although free fatty acids are the main constituents of lipids, they are predominantly found esterified to a glycerol molecule in the form of glycerides. The glycerol molecule forms the backbone of the glyceride and contains one, two or three fatty acids, each esterified to one of the carbon atoms of the glycerol (Figure 4.3). Although often called mono-, di- and triglycerides, these are more correctly called mono-, di- and triacylglycerols.

After refining, most natural fats are predominantly triacylglycerols (TAG), containing anywhere between 95% and 99% TAG with only a few percent of other lipids. Minor components found in natural fats may include free fatty acids, mono- (MAG) and diacylglycerols (DAG), phospholipids, sterols, and others. Although these minor lipid components can influence lipid properties, it is the composition of TAG that predominantly govern the properties and chemical reactivity of natural fats.

The specific fatty acids that are present and their arrangement on the glycerol molecule determine the chemical and physical properties of the fat. The three C atoms of the glycerol molecule are termed as *sn*-1, *sn*-2 and *sn*-3. Consider how three fatty acids could be randomly arranged on the glycerol molecule; there would be 3 × 3 or nine potentially different TAG structures that can be formed. However, since the TAG is symmetric around the center carbon in the glycerol molecule (*sn*-2 position), not all of the TAG structures are distinct. Fortunately, nature is not always completely random when designing natural fats and the actual number of TAG is generally not as high as complete randomness would allow. Cocoa butter is one the simplest natural fats, with three TAGs that dominate its composition, but even it contains at least 20 different TAGs. Milk fat is probably the most complex natural fat, containing well over 200 different TAGs (although none are present at greater than 5% on a molar basis).

Because of the diverse chemical composition, it is often difficult to accurately characterize (and analyze) the TAG composition of natural fats. One way to characterize natural fats is to separate TAG according to the number of unsaturated fatty acids they contain. Table 4.2 shows the breakdown of TAG in terms of saturation for several natural fats of importance in confections. Such information can be used as a guideline to the properties of the fats. Palm oil and cocoa butter, for example, contain a high concentration of TAG with only one unsaturated fatty acid, whereas peanut and soybean oils contain a high content of TAG with two or even three unsaturated fatty acids (and some of these may even be polyunsaturated fatty acids). It is this difference in composition that leads to differences in physical properties, such as the melting point. For this reason, palm oil and cocoa butter are solid at normal room temperature (fats), whereas soy and peanut oil are liquid (oils).

More complete description of lipid chemistry requires knowledge of the individual TAG species present. However, since most natural fats contain

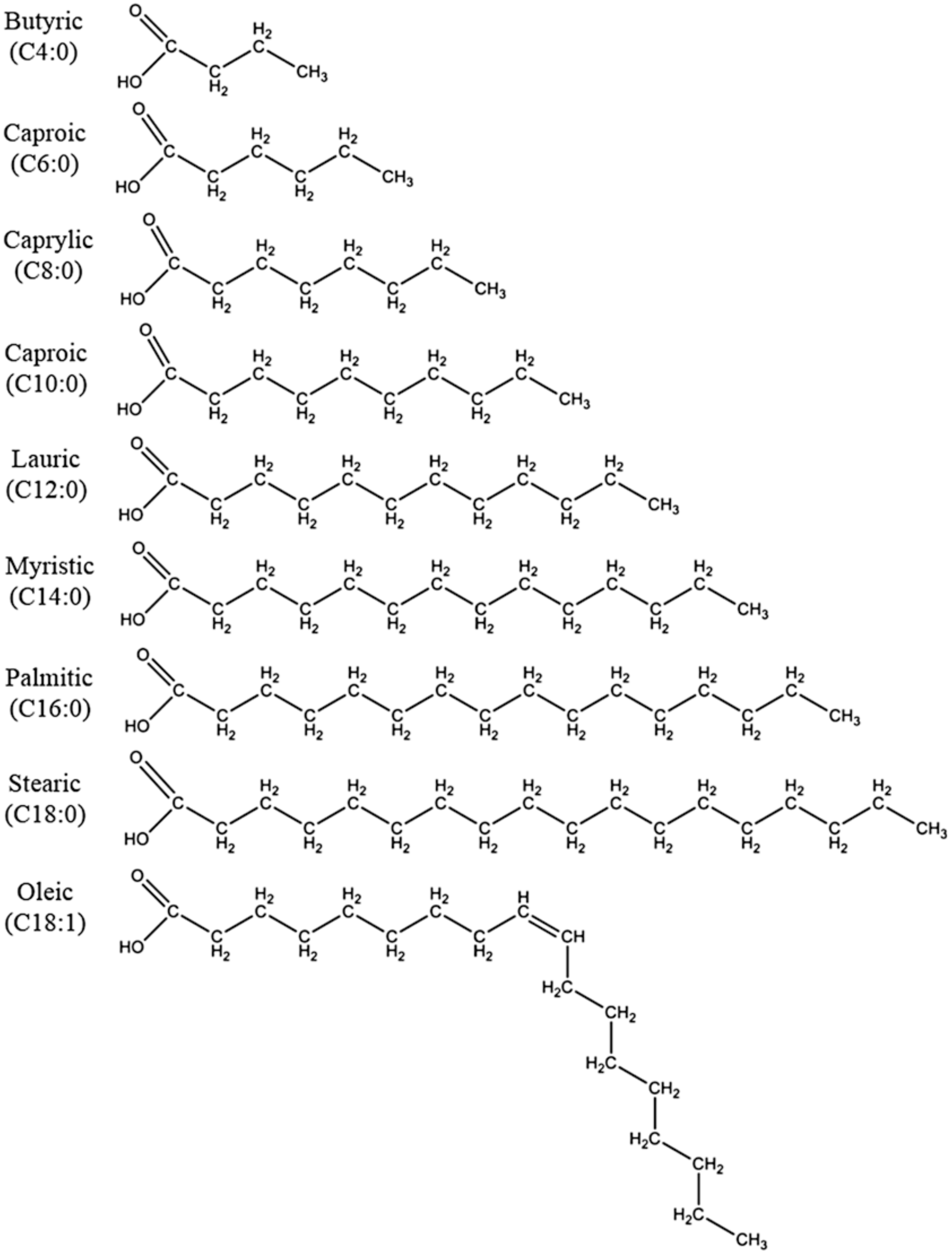
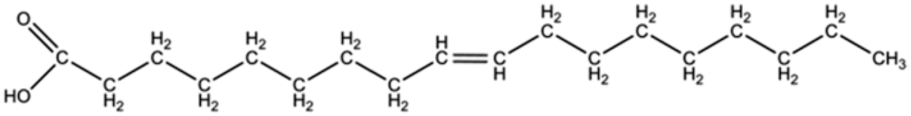
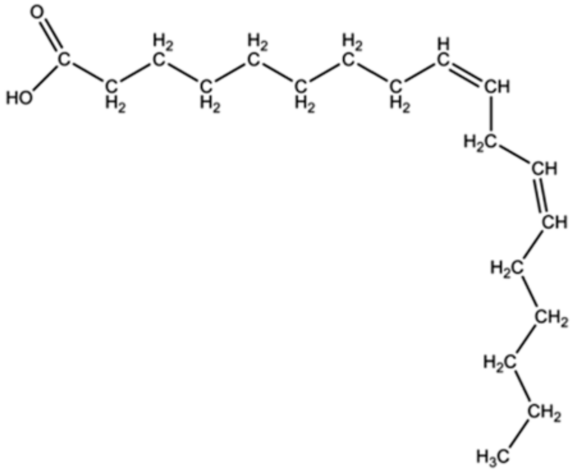


Figure 4.2 Common fatty acid structures

Elaidic
(C18:1*trans*)



Linoleic
(C18:2)



Linolenic
(C18:2)

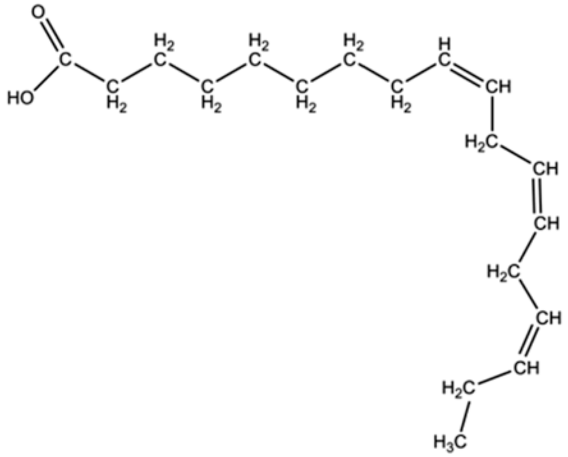


Figure 4.2 (continued)

numerous different TAG distinguished only by small differences (carbon chain length) in molecular characteristics, complete separation of each individual TAG in natural fats has traditionally been difficult. Modern analytical techniques (Lipp and Anklam 1998b; Lipp et al. 2001) now allow adequate separation of the majority of the different species of natural fats. This degree of separation of TAG species allows detection of most, but not all, cases of adulteration of cocoa butter with other fats. Furthermore, the specific chemical composition of natural fats like cocoa butter is not always the same for each and every cocoa butter, but depends on many factors, including cacao species, country of origin, and environmental conditions during growth.

Composition of TAG in cocoa butter and their ranges are shown in Table 4.3. Variations arise from differences in growth conditions and type of cacao. The predominant TAGs in cocoa butter are monounsaturated, with oleic acid in the middle (*sn*-2) position of the glycerol molecule and

Table 4.1 Fatty acid composition[a] (in %) of various natural fats used in confections

Fatty acid		Milkfat	Cocoa butter	Illipe butter	Palm oil	Palm kernel oil	Soybean oil	Peanut oil	Coconut oil
Butyric (Bu)	C4:0	3.8	–	–	–	–	–	–	–
Caproic (C)	C6:0	2.3	–	–	–	0.3	–	–	0.5
Caprylic (Cy)	C8:0	1.1	–	–	–	3.9	–	–	8.0
Capric (Ca)	C10:0	2.0	–	–	–	4.0	–	–	6.4
Lauric (La)	C12:0	3.1	–	–	0.3	49.6	–	–	48.5
Myristic (M)	C14:0	11.7	0.1	–	1.1	16.0	0.1	0.1	17.6
Palmitic (P)	C16:0	26.2	25.8	19.5	45.1	8.0	11.0	11.6	8.4
Stearic (S)	C18:0	12.5	34.5	42.4	4.7	2.4	4.0	3.1	2.5
Oleic (O)	C18:1	28.2	35.3	36.9	38.8	13.7	23.4	46.5	6.5
Linoleic (L)	C18:2	2.9	2.9	0.2	19.4	2.0	53.2	31.4	1.5
Linolenic (Li)	C18:3	0.5	–	–	0.3	–	7.8	–	–

[a] Source: Minifie (1989)

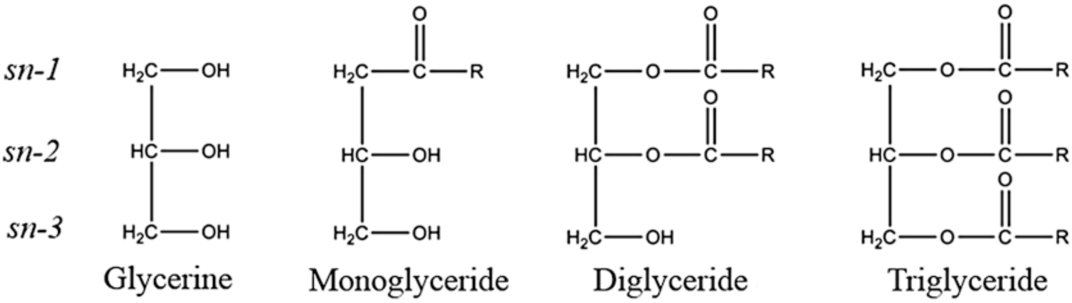


Figure 4.3 Glyceride structures, where *R* can be any aliphatic chain

Table 4.2 Triacylglycerol (TAG) class content, based on degree of saturation (but not placement on the glycerol molecule), for some natural fats

TAG[a]	Palm[b]	Peanut[b]	Cottonseed[b]	Soy[c]	Palm kernel[c]	Coconut[c]	Cocoa butter[d]
SaSaSa	7.9	–	0–0.1	0	76	81	2.5–3.0
SaUnSa	42.8	1.0	13.2–14.0	6	15	12	74.0–85.0
SaSaUn	6.6						
$SaUn_2$	35.7	56.0	50.0–58.0	38	9	7	13.0–20.0
Un_3	6.8	43.0	28.0–36.0	56	0	0	1.0

[a] *Sa* saturated, *Un* unsaturated
[b] Source: O'Brien (1998)
[c] Source: Bockisch (1998)
[d] Source: Minifie (1989)

either stearic or palmitic acids on the two outside carbons. These monounsaturated TAG make up about 70–85% of the TAG composition of cocoa butter. However, the remaining TAG, particularly those with lower melting points, play an important role in the physico-chemical properties of solidified cocoa butter.

While cocoa butter is arguably one of the simplest natural fats, milk fat is easily one of the most complex in terms of number of TAG species. Over 200 different TAG have been measured (Gresti et al. 1993) and many more are present at very low concentrations. Milk fat is quite unique in that there is no predominant TAG

Table 4.3 Triacylglycerol (TAG) composition ranges (in % area of chromatographic peaks) for cocoa butter. The ranges are due to different cocoa butter origins

TAG[a]	Double bonds	Acyl carbon[b] number	Cocoa butter[c]
POS	1	52	34.6–38.3
SOS	1	54	23.7–28.4
POP	1	50	13.8–16.4
SOO + PPP	0 or 2	54 or 48	3.7–8.4
POO	2	52	2.2–5.5
PSL	2	52	2.8–3.6
SOA	1	56	1.6–2.5
SSL	2	54	1.5–2.1
PPL	2	50	1.5–1.9
OOA	2	56	1.0–1.6
POL	3	52	0.6–1.1
SSP	0	52	0.2–1.3
SOL	3	54	0.4–1.0
OOO	3	54	0.2–0.9
PPS	0	50	0.3–0.7
MOO + MMP	0 or 2	50 or 46	0.2–0.5

[a] *P* palmitic, *O* oleic, *S* stearic, *M* myristic, *L* linoleic, *A* arachidonic acids

[b] Acyl carbon number – sum total of carbons in all fatty acids

[c] Source: Lipp and Anklam (1998a)

that crystallizes as a group. As seen in Table 4.4, the ten most abundant TAG are present at less than 5% of the total TAG. This composition leads to unique solidification properties of milk fat and affects the mixing behavior when milk fat is combined with other fats (as in milk chocolate).

The TAG composition of some other important confectionery fats, including palm oil, palm kernel oil, coconut oil and peanut oil, are given in Tables 4.5, 4.6, 4.7, and 4.8, respectively. Tables 4.3, 4.4, 4.5, 4.6, 4.7, and 4.8 clearly document the differences in chain length, degree of unsaturation and TAG arrangement of these various fats, reflecting the fat's source and environmental growth factors. As it will be seen later, these compositional differences are what lead to vast physico-chemical differences of these fats in confectionery applications, from melting profiles to stability during shelf life.

Table 4.4 Concentration (mole%) of the ten most prevalent triacylglycerols (TAG) in milk fat

TAG[a]	Double bonds	Acyl carbon[b] number	Milk fat[c]
BPO	1	38	4.2
BPP	0	36	3.2
BMP	0	34	3.1
MPO	1	48	2.8
POO	2	52	2.5
BPS	0	38	2.5
PPO	1	50	2.3
PSO	1	52	2.2
CPO	1	40	2.0
BMO	1	36	1.8

[a] *B* butyric acid (C4:0), *C* caproic acid (C6:0), *M* myristic acid (C14:0), *P* palmitic acid (C16:0), *S* stearic acid (C18:0), *O* oleic acid (C18:1)

[b] Acyl carbon number – sum total of carbons in all fatty acids

[c] Sources: Hartel and Kaylegian (2001) and Gresti et al. (1993)

Table 4.5 Triacylglycerol (TAG) composition (in %) of palm oil

TAG[a]	Double bonds	Acyl carbon[b] number	Palm oil[c]
POP	1	50	24.1
POO	2	52	18.9
PLP	2	50	7.8
POS	1	52	7.0
OOL,OLO,PLL	2–4	52–54	5.7
MLO, PLO, SLO	1	52–54	5.4
MOL, POL, SOL	1	50–52	4.8
PPP	0	48	4.3
PPO	1	50	3.6
SOO, MOO	2	50–52	3.4
MLP, SLP, PPL	2	50–52	3.3
OOO	3	54	2.7
PMP, MPP, PPS, PSP	0	46–50	2.0
SPO, PSO, SSO	1	52–54	1.7
MOP	1	48	1.2
SPL, SSL, SLS	2	54	0.7
SOS	1	54	0.5
SSS, SPS, PSS	0	52–54	0.3
Other	–	–	1.7

[a] *M* myristic acid (C14:0), *P* palmitic acid (C16:0), *S* stearic acid (C18:0), *O* oleic acid (C18:1), *L* linoleic acid (C18:2)

[b] Acyl carbon number – sum total of carbons in all fatty acids

[c] Sources: Bockisch (1998)

Table 4.6 Triacylglycerol (TAG) composition (in %) of palm kernel oil

TAG[a]	Double bonds	Acyl carbon[b] number	Palm kernel oil[c]
LaLaLa, CaLaM	0	36	27
LaLaM	0	38	25
LaLaP, LaMM	0	40	15
MMM	0	42	9
CaLaLa, CaLaM	0	34–36	6
CaLaLa	0	34	3
LaPS, MPP, MMS	0	46	3
MOP	1	48	3
PPO	1	50	1
POS	1	52	1
SOS	1	54	1
LaOO, OLaO	2	48	1

[a] *Ca* capric (C10:0), *La* lauric acid (C12:0), *M* myristic acid (C14:0), *P* palmitic acid (C16:0), *S* stearic acid (C18:0), *O* oleic acid (C18:1)
[b] Acyl carbon number – sum total of carbons in all fatty acids
[c] Sources: Bockisch (1998)

4.2.1.3 Other Lipids

Although TAGs are the main components of importance in natural fats, the minor components may sometimes be important to the physicochemical properties of the fat. The minor lipids include free fatty acids, mono- and diglycerides, sterols, tocopherol, and phospholipids, among others. These components can potentially influence polymorphic behavior and crystallization rates through their interactions either at the crystal surface or through incorporation into the crystal lattice. Since these minor lipids also tend to be more polar than TAG, they may also have surface-active properties that influence rheological properties of the fats, particularly in dispersions found in chocolate and compound coatings.

As an example, Table 4.9 shows the minor lipid composition of modified palm kernel oil, two different versions of anhydrous milk fat, and cocoa butter. In general, the more highly refined the fat, the lower the content of minor lipids.

Table 4.7 Triacylglycerol (TAG) composition (in %) of coconut oil

TAG[a]	Double bonds	Acyl carbon[b] number	Coconut oil[c]
LaLaM, LaMLa	0	38	11–15
LaMP	0	42	3–13
LaLaLa	0	36	5–12
CyLaLa	0	32	2–8
CaLaLa	0	34	5.5–10
CyLaM	0	32	1.5–10
CaLaM	0	34	7.5–9
LaLaP, LaPLa	0	40	4–7.5
CyLaO	1	38	2.5–5.5
CaLaP	0	38	1.5–5
CaLaO	1	40	1.5–4
LaMO	1	44	1.4–4
CyLaP	0	36	2.5–3.5
LaLaO, LaOLa	1	42	0.5–3
LaPO	1	46	1–2
CaMP	0	40	0.5–1
CyPO	1	42	0.5
CaPO	1	44	0.5

[a] *Cy* caprylic acid (C8:0), *Ca* capric (C10:0), *La* lauric acid (C12:0), *M* myristic acid (C14:0), *P* palmitic acid (C16:0), *S* stearic acid (C18:0), *O* oleic acid (C18:1)
[b] Acyl carbon number – sum total of carbons in all fatty acids
[c] Sources: Bockisch (1998)

4.2.2 Chemical Properties

Several characteristics of natural fats, based on the chemical composition, are important to the confectioner. These properties determine the characteristics of a fat in a specific candy application and determine whether or not a certain fat can be used in that application. An obvious example is that a vegetable oil (liquid at room temperature) cannot be used to make chocolate coating unless the chemical composition of that vegetable oil has been modified in some way.

4.2.2.1 Free Fatty Acid Content

The level of free fatty acids (FFA) found in a natural fat is indicative of either enzymatic or chemical reactions that cause hydrolysis of fatty

Table 4.8 Triacylglycerol (TAG) composition (in %) of peanut oil

TAG[a]	Double bonds	Acyl carbon[b] number	Peanut oil[c]
LOO, OLO	4	54	19.4
OLL	5	54	18.3
POL	3	52	12.9
OOO	3	54	11.8
POO	2	52	6.7
PLP	2	50	5.3
PLL	4	52	5.1
SOL	3	54	3.9
PPL	2	50	2.9
POP	1	50	2.3
PSO	1	52	2.2
LOL	5	54	2.2
LLL	6	54	2.0
SOO	2	54	1.5
SLL	4	54	1.4
Others	>5	–	0.5

[a] *M* myristic acid (C14:0), *P* palmitic acid (C16:0), *S* stearic acid (C18:0), *O* oleic acid (C18:1), *L* linoleic acid (C18:2)

[b] Acyl carbon number – sum total of carbons in all fatty acids

[c] Sources: Bockisch (1998)

Table 4.9 Minor lipid composition (in %) of cocoa butter, milk fat and fractionated palm kernel oil

Lipid class[a]	Cocoa butter[b]	FPKO[c]	WAMF[d]	SAMF[d]
TAG	96.8 ± 0.1	99.3 ± 0.6	98.0 ± 0.1	98.0 ± 0.3
FFA	1.8 ± 0.0	0.32 ± 0.19	0.94 ± 0.06	0.70 ± 0.11
1,3-DAG	1.0 ± 0.0	0.02 ± 0.04	0.59 ± 0.10	0.74 ± 0.16
1,2-DAG	0.3 ± 0.0	Not measured	0.28 ± 0.05	0.21 ± 0.07
MAG	Trace	0.36 ± 0.57	0.04 ± 0.03	0.08 ± 0.05
Sterol	0.1 ± 0.0	0.01 ± 0.02	0.18 ± 0.02	0.21 ± 0.07

[a] *TAG* triacylglycerol, *FFA* free fatty acid, *1,3-DAG* 1,3 diacylglycerol, *1,2-DAG* 1,2 diacylglycerol, *MAG* monoacylglycerol

[b] Source: Tietz and Hartel (2000)

[c] *FPKO* fractionated palm kernel oil; source: Schmelzer and Hartel (2001)

[d] *WAMF* winter anhydrous milk fat, *SAMF* summer anhydrous milk fat; source: Schmelzer and Hartel (2001)

acids from TAG. FFA levels may vary from 2% to 3% in unrefined oils to less than 0.1% in highly refined oils. FFA can have significant negative effects on lipid characteristics. Most notably, high FFA levels are often associated with disagreeable odor, especially for shorter chain fatty acids, but they may also affect crystallization and phase behavior.

4.2.2.2 Iodine Value

The relative ratio of unsaturated to saturated fatty acids in a natural fat is given quantitatively by the Iodine Value (IV). Fats that have high content of saturated fatty acids have low IV values and conversely, highly unsaturated fats have very high IV values. Of primary importance, the IV value is a relative indicator of oxidative stability since saturated fatty acids are much less susceptible to oxidation than unsaturated fatty acids. Thus, a fat with a high IV is more prone to rancidity than a fat with lower IV. On the other hand, the IV value is also a general indicator of physical properties, since saturated fatty acids have higher melting points than unsaturated fatty acids. Thus, lipids with low IV tend to be fats (solid at room temperature) and those with high IV tend to be oils (liquid at room temperature). The iodine value range is often used to help indicate the base material of the fat or oil. Typical IV values for confectionery fats vary from as low as 10 to greater than 100 (Table 4.10).

4.2.2.3 Refractive Index

Liquid oils refract light depending on the fat composition in the same way that sugar solutions refract light based on sugar type and concentration (see Section 2.5). In general, refractive index of oils tracks closely with IV. For this reason, refractive index is generally used as an indicator of extent of hydrogenation. Refractive index values of confectionery fats are also given in Table 4.10.

4.2.2.4 Peroxide Value

Peroxides are produced as one of the early products of lipid oxidation, as a result of the reaction

Table 4.10 Properties of confectionery fats

Fat	Refractive index	Iodine value	Melting point (°C)
Soybean oil	1.470–1.476[a] (25 °C)	123–139[a]	−23.0 to −20.0[a]
Cottonseed oil	1.468–1.472[a] (25 °C)	99–113[a]	10.0–16.0[a]
Peanut oil	1.467–1.470[a] (°25 °C)	84–100[a]	−2.0[a]
Palm oil	1.4565–1.4585[a] (40 °C)	51–55[a]	30.0–38.0[a, b]
Palm olein	–	51–61[a]	19.0–24.0[a, b]
Palm stearin	–	22–50[a]	44.0–56.0[a, b]
Coconut oil	1.448–1.450[a] (40 °C)	7.5–10.5[a]	23.0–26.0
Palm kernel oil	1.448–1.452[a] (40 °C)	13–23[a]	24.0–26.0[a]
Milk fat	1.4465[a] (40 °C)	25–42[a]	28.0–36.0[a, c]
Cocoa butter	1.456–1.458[d] (40 °C)	35–40[d]	32.8–35.0[d]

[a] Source: O'Brien (1998)
[b] Softening point
[c] Mettler dropping point
[d] Source: Minifie (1989)

between oxygen and unsaturated fatty acids. For this reason, peroxide value (PV) is often used to indicate how much oxidation has occurred in a fat. PV is determined as the concentration of substances that oxidize potassium iodide to iodine and is expressed in milli-equivalents of peroxide per kg of sample. In general, higher PV values indicate greater oxidation and deterioration of a fat sample. However, since peroxides are broken down further into degradative components such as FFA's, PV initially increases with oxidation level before decreasing again as further oxidation of the fat occurs. For this reason, PV is not always a good indicator of lipid oxidation. A high PV value is a good indicator of off-flavors, but a fat with low PV value may have undergone significant oxidation and be high in rancid off-flavors.

4.2.3 Lipid Oxidation

In confections, there are several important chemical reactions that can take place in lipids either during processing or during storage that can influence product quality (Padley 1994). Probably the most important of these is lipid autoxidation, which causes rancid, off-flavors to form. Exposure to light, particularly UV light, can cause photo-oxidation. The off-flavors formed by enzymatic lipolysis can also cause problems during storage of some confections. Timms (2003) also mentions ketonic rancidity of lauric fats, caused by molds in the presence of moisture and oxygen.

4.2.3.1 Autoxidation

In the presence of oxygen, lipids can be oxidized to produce volatile compounds that contribute to a rancid off-flavor/odor. Autoxidation involves a complex, autocatalytic series of reactions involving formation of hydroperoxide radicals, which then further cause oxidation as they migrate through the oil. The hydroperoxides themselves react to form aldehydes, ketones and free fatty acids, among other chemical products. These compounds, being quite volatile, impart an undesirable rancid off-flavor/odor to the fat, which typically increases with storage time. Since unsaturated fatty acids undergo oxidation at a much greater rate than saturated fatty acids, fats with a higher IV value are typically more sensitive to off-flavor development during storage. For example, linolenic acid (C18:3) undergoes oxidation two times faster than linoleic acid (C18:2), 25 time faster than oleic acid (C18:1) and 2,500 times faster than stearic acid (C18:0) (Bockisch 1998). Thus, coconut oil (IV ≈ 8) and palm kernel oil (IV ≈ 13) are significantly less prone to oxidation than peanut oil (IV ≈ 100).

In confections, oxidation of peanut oil is one of the main concerns governing the shelf life of peanut-containing products. Peanut oil contains approximately 32% (range 13–45%) linoleic acid (C18:2) and 46.7% (range 36–72%) oleic acid. Because of the high linoleic acid content, autooxidation of peanut oil occurs rapidly. New varieties of peanut with high oleic acid content have been developed to reduce the rate of oxidation and extend shelf life of peanut-containing products. As an example, Mugendi et al. (1998) found the oxidation rate of two high oleic acid peanut varieties (oleic acid: 80% and linoleic acid: 3%) to be about ten times less than a regular variety peanut oil (with 27% linoleic and 53% oleic acid).

In addition to fatty acid composition, numerous factors serve to promote oxidation. Increased levels of oxygen, elevated temperatures (hold melted fats at about 10 °F above MP for longer shelf life), and the presence of water all have been found to promote autoxidation. Likewise, the presence of metal catalysts (copper, iron, manganese and nickel) promotes autoxidation and formation of rancid off-flavors. Even processing of lipids in metal vessels, particularly copper vessels, has been found to promote autoxidation. In some fats, however, the presence of natural antioxidants can inhibit oxidation, making them more resistant to oxidation during storage than might be predicted based on their IV number. Naturally occurring tocopherols, for example, are known to inhibit oxidation, although the addition of BHA/BHT or TBHQ also serves the same purpose.

4.2.3.2 Photooxidation

Oxidative rancidity can also be generated by exposure to light (whereas autooxidation can occur even in the dark). Here, singlet oxygen is generated by photosensitization of certain components, primarily natural pigments, in foods. In the past, photooxidation has been of limited concern to the confectioner, but with the increased use of natural colors and flavors, it may see greater importance.

4.2.3.3 Lipolysis (Hydrolytic Oxidation)

The presence of certain types of enzymes, called lipases, can cause breakdown of TAG into the substituent fatty acids, which leads to rancid off-flavors and odors. These enzymes are often introduced into confections through molds associated with certain ingredients (e.g., nuts) or may be present in milk products or spices. Storage at warm, but not hot, temperatures promotes lipase activity and hydrolytic oxidation. Some water is also necessary for lipolysis; however, lipases are known to be active even at moisture levels less than 1%.

Fats with shorter chain fatty acids are more prone to rancidity problems from lipolysis due to their characteristic odors even at very low levels. Milk fat, in particular, has numerous short-chain fatty acids that lead to rancid off-flavors. The threshold level of butyric acid is only 6 ppm (Hogenbirk 1987), meaning very low levels of oxidation can cause significant problems. Lauric fats (coconut and palm kernel oil) also have lower tolerance for lipolytic rancidity due to the soapy characteristic of free lauric acid. The threshold level for detection of lauric acid is 700 ppm (Hogenbirk 1987). Oxidation of stearic acid is generally not a problem since the threshold level for sensory detection is 15,000 ppm (Hogenbirk 1987). Lipolytic rancidity can be prevented by deactivating lipases by exposure to temperatures greater than 180 °F.

4.3 Physical Properties

The physical properties of fats are closely tied to the molecular arrangement and their crystallization behavior. Solidification of fats is more complex than that of sugars (see Section 2.10), due in part to the complex molecular make-up of lipids, but also due to the ability of lipid molecules to form more than one crystal form, a phenomenon known as polymorphism.

4.3.1 Polymorphism

When fats crystallize, TAG molecules can come together in different crystalline forms, called polymorphs. The flexibility of TAG molecules allows them to form into different crystal lattice structures, each with different stability. Lipid polymorphs are distinguished by differences in molecular packing (single or double spacing) and the angle of the fatty acid moieties on the TAG within the crystal lattice.

Specifically, fats exhibit what is called monotropic polymorphism, where less stable polymorphs are formed first and subsequently transform into more stable states. It is generally accepted that there are three main polymorphic forms for fats, typically given the designation of α, β' and β, in increasing order of stability

(Figure 4.4a). However, there may be other metastable polymorphs that form under certain conditions and in certain fats. These have been variously called γ, δ, or sub-α. There may also be sub-classes of the polymorphic forms, as in the two β polymorphs observed in cocoa butter (Loisel et al. 1998). The complex polymorphic behavior of cocoa butter is shown in Figure 4.4b. A summary of the different polymorphic forms found in a variety of fats can be found in D'Souza et al. (1990) and Sato et al. (1999).

In polymorphs of lower stability (α), the TAG molecules are arranged in a relatively loose crystal lattice where the molecules are not packed together very tightly in the crystal structure. In contrast, the most stable β polymorph has the TAG molecules arranged in the tightest possible packing arrangement, with the lowest energy state. This difference in packing arrangement between the polymorphs means there are certain differences in physical properties. For one, the melting point increases with polymorph stability, so the α polymorph has lower melting point than that of the β′ polymorph, which is lower than that of the β polymorph. The difference in packing arrangement also leads to differences in latent heat released upon melting (or crystallization), with the highest latent heat found for the most stable, β, polymorph. These differences in melting point and latent heat (ΔH) are shown for various simple (a single fatty acid) TAG in Table 4.11. In general, TAG with shorter chain length and unsaturated fatty acids have significantly lower melting point and release less latent heat than TAG with longer chain length and saturated fatty acids. The increased melting temperature occurs

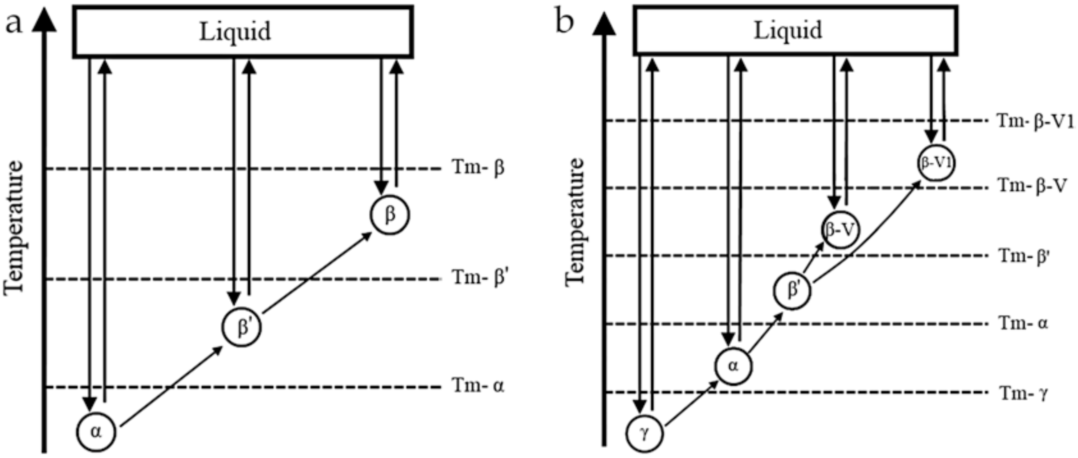


Figure 4.4 Monotropic polymorphism of fats: **a**) general polymorphic trends; **b**) polymorphic behavior of cocoa butter.

Table 4.11 Melting points and latent heats of fusion (ΔH) for different polymorphs of some monoacid triacylglycerols (TAG)

TAG[a]	Melting temperature (°C)[b]			Latent heat (kJ/mole)[b]		
	α	β′	β	α	β′	β
SSS	54.7–55.0	61.0–64.0	73.0–73.5	109.3–112.2	142.8	188.4–191.8
PPP	44.7–46.0	53.0–56.6	66.0–66.4	93.4–103.0	131.5	163.3–165.8
MMM	31.0–32.8	41.0–51.0	56.0–58.5	78.7–85.0	100.5	135.2–136.9
LaLaLa	14.0–15.2	30.0–40.0	46.0–46.5	60.3–72.0	81.2	114.3–116.4
OOO (*cis*)	(−32.0)–(−37.0)	(−5.0)	(−2.5)–5.5	NA	NA	95.6–113.1
OOO (*trans*)	15.0–16.6	37.0	41.0–42.0	NA	NA	133.5–148.3

[a] *La* lauric acid, *M* myristic acid, *P* palmitic acid, *S* stearic acid, *O* oleic acid
[b] Source: Hageman (1988)

because longer-chain fatty acids interact over a larger number of carbon atoms.

In monotropic polymorphism, lower stability polymorphs are formed first (higher nucleation rates), usually when the fat is cooled to lower temperatures (Figure 4.4a). The specific polymorph that forms first depends on the nature of the fat, the cooling rate and temperature, and shearing rate (high shear conditions can lead to formation of more stable polymorphs than expected in the absence of high shear). Unstable forms then gradually transform to more stable polymorphs at a rate dependent on temperature, the nature of the molecular structure, and the presence of impurities. For example, if a liquid fat is cooled to a temperature below the melting point of the β′ polymorph, generally it will crystallize in the β′ form. The β′ polymorph then generally transforms to the more stable β polymorph. At lower temperatures the time for polymorphic transformation is longer than at higher temperatures. Of course, if the melting temperature of the lower stability polymorph is exceeded, it quickly melts and transforms to the more stable polymorphic form. This behavior is used to advantage during tempering of chocolates to develop the desired β polymorph.

Although the β form is the most stable of lipid polymorphs, due to the complex molecular distribution in some natural fats, only the β′ polymorph may appear. The complex mixture of TAG and their differences in chain length and degree of unsaturation make them incompatible with the stable β polymorph crystal structure. For example, the wide array of TAG molecules that make up milk fat prevent formation of the tightest packing arrangement in the β polymorph and only the β′ polymorph is observed even after long-term storage. The most stable polymorphic forms observed for various natural fats are listed in Table 4.12. Interestingly, although the β polymorph is the most stable form for palm kernel oil, it is generally found in the β′ polymorph when used in compound coatings. This is discussed in further detail in Chapter 16, since this polymorphic transition seems to affect bloom formation in compound coatings made with palm kernel oil.

Table 4.12 Most stable polymorph found in various natural fats

β-forming	β′-forming
Cocoa butter	Milk fat
Lard	Palm oil
Palm kernel oil	Cottonseed oil
Sunflower oil	Menhaden oil
Canola oil	Rapeseed oil
Coconut oil	Tallow
Olive oil	
Peanut oil	
Safflower oil	
Soybean oil	

Source: O'Brien (1988)

Polymorphism in fats is most often quantified by using x-ray spectroscopy. When x-rays are passed through a crystalline fat (or any crystalline material, for that matter), the regular alignment of the atoms within the crystal lattice causes scattering of the x-rays, which produces a well-defined scattering spectrum that is related to the molecular arrangement within the lattice. Thus, the x-ray scattering spectrum can differentiate the polymorphs based on the scattering intensities. The α polymorph is characterized by a strong peak near 4.5 Å, which is associated with the short spacing (distance between adjacent molecules in the lattice). The β′ polymorph has two short spacing peaks near 3.8 and 4.2 Å, whereas the β polymorph generally has a strong peak near 4.6 Å and two weaker peaks at 3.8 and 5.4 Å. Hernqvist (1988) provides more details on lipid crystal structures and x-ray analysis of polymorphic forms of fats.

In some materials, the polymorphic behavior is more complex than can be described by the simple α, β′ and β description. More than one polymorph may be found within a category, as seen in cocoa butter (Figure 4.4b). Even though numerous detailed scientific studies have investigated the exact polymorphic nature of cocoa butter, there still is some debate about the true distinction of the polymorphic forms. Depending on the study, there are either five or six distinct polymorphic forms, some of which exhibit a range of melting temperatures dependent on specific molecular make-up and processing condi-

Table 4.13 General classification of polymorphic forms of cocoa butter

Polymorphic form[a]		Melting point[b] (°C)	Comments
I	Sub-α	17.3	
II	α-2	23.3	
III	β_2'-2	25.5	van Malssen et al. (1999), and others, argue that form III is not a unique form
IV	β_1'-2	27.5	van Malssen et al. (1999) also claim there is only one β' form, which has a range of melting temperatures from 20 to 27 °C
			Typically the polymorph that forms first in untempered chocolate.
V	β_2–3	33.8	Polymorph typically found in well-tempered chocolate
VI	β_1–3	36.2	Associated with chocolate bloom

[a] In Greek nomenclature, subscript gives order of stability (1 is most stable within category) and hyphenated number defines packing arrangement of fatty acids, with 2 being double chain packing and 3 triple chain packing

[b] Source: Wille and Lutton (1966)

tions (Timms 2003; Talbot 2009; Windhab 2009). The different polymorphic forms of cocoa butter are briefly summarized in Table 4.13. Each polymorph has a different melting temperature, with increasingly stable polymorphs having higher melting temperature. The desired polymorphic form in chocolate is Form V (or stable β_2 form), often called the β V polymorph. Note that this is not the most stable form for cocoa butter, and in fact, formation of the most stable polymorph (Form VI, or β_1, often called β VI) is generally associated with the formation of fat bloom (although fat bloom is not necessarily caused by this polymorphic transition). Section 15.5.5 provides more details on crystallization and polymorphism of cocoa butter, as related to tempering of chocolate, and Section 15.6.1 covers factors related to bloom formation and shelf life.

4.3.2 Phase Behavior

The phase behavior of fats, or the relationships between solid and liquid phases, is related to the molecular make-up of the fat. The important phase-related properties of confectionery fats include final melting point, melting profile (including solid fat curve), and phase mixing behavior of fat blends.

Typically, fat is considered to be a "melt" system like water. At temperatures above the melting point, the material is liquid. The melt point is the temperature above which all crystalline material becomes liquid (although at a rate dependent on molecular disorganization from the crystal lattice). When a melt system is cooled below the melting point, there is a crystallization temperature below which the material quickly becomes crystalline. In the region between the melting and crystallization temperatures, the material may remain as a sub-cooled liquid for a period of time due to the kinetic constraints related to formation of a crystal nucleus. For example, pure water may be sub-cooled to as low as −40 °C without nucleation (for homogeneous nucleation), although typically, this sub-cooling range is only about −6 °C (for heterogeneous nucleation). Note that there is a kinetic effect as well, where over long times, a sub-cooled melt system may eventually nucleate. This type of phase behavior is also seen for pure TAGs, which are liquid above the melting point and crystallize at temperatures below the crystallization temperature with a rate depending on the nature of the molecule and the surrounding conditions (agitation, cooling rate, etc.).

However, natural fats contain a range of TAG, each with their own melt point temperature. As temperature of a natural fat is decreased, more and more of the TAG molecules become sub-cooled (below their individual melt temperature) and can participate in crystallization. Thus, natural fats exhibit a melting point range, rather than a single melting point temperature. Furthermore, mixtures of natural fats, with complex TAG distributions, exhibit complex phase behavior dependent on the nature of all the different molecules in the mixture. For example, milk fat and cocoa butter each have numerous different TAG when found together in milk chocolate and the mixture has even more complex phase behavior than each of the two fats by themselves.

4.3.2.1 Melting Point

The temperature at which a pure TAG melts is dependent on the fatty acid composition and the arrangement of the fatty acids on the glycerol molecule, as seen in Table 4.11. TAG with short-chain (trilaurin) and unsaturated fatty acids (triolein) have lower melting points, whereas those with long-chain saturated fatty acids (tristearin) have higher melting temperatures. Increasing chain length (trilaurin, trimyristin, tripalmitin and tristearin) leads to an increase in melting point. TAG composed of *trans* unsaturated fatty acids have higher melting points than those with fatty acids in the *cis* form. This is because *trans* unsaturated fatty acids have a more straight, only slightly kinked, molecular conformation rather than the bent conformation seen with *cis* unsaturated fatty acids (Figure 4.2).

For pure TAG with mixed fatty acids, melting point depends on which fatty acids are present and the arrangement of the fatty acids on the glycerol molecule. In general, the more unsaturated fatty acids and shorter chain fatty acids present on a TAG, the lower the melting point temperature.

Natural fats are comprised of various mixed TAG (Tables 4.3, 4.4, 4.5, 4.6, 4.7, and 4.8), each with their own individual melting point. Thus, natural fats exhibit a range of melting temperatures based on their TAG composition. That is, as temperature decreases, first the TAG with highest melting points solidify with additional TAG solidifying as temperature decreases below their melting points. In reality, it is much more complicated as the various TAG interact and crystallize together, resulting in complex crystallization and melting behavior (see next section). Looking at it from the other direction, as temperature of a solidified fat increases, more and more TAG melt as their melting point is surpassed. Ultimately, it is the temperature at which the highest melting lipid component melts, within the mixture of different TAG, that determines the final melting point temperature of the fat.

Melting point has been measured in various ways over the years. Any specification of the melting point temperature of a natural fat should be accompanied by the method of measurement since each method gives slightly different results (by up to a few °C). Melting points are often given as clear point, softening point, slip point, Wiley melting point or dropping point (O'Brien 1998).

The clear point (or capillary melting point) is defined as the temperature at which the last remnants of crystals just disappear under controlled melting conditions (AOCS 1994 Method Cc 1–25). The point at which the last fat crystal is visually seen to melt within a closed capillary tube is marked as the clear point. The softening point is the temperature at which the fat first slips in the capillary tube (AOCS 1994 Method Cc 3–25). This temperature marks the point where sufficient melting has occurred to cause the liquid to flow. Slip point is generally several degrees lower than the clear point since some solid fat is still left when the slip point is reached. Wiley melting point (AOCS 1994 Method Cc 2–38) and Mettler (Mettler Instruments, Co.) dropping point (AOCS Method 1994 Cc 18–80) are two common methods of measuring the point where sufficient melting has taken place for flow to occur. Since the Mettler dropping point apparatus is fully automated and simple to use, it has become the industry standard.

Melting points (dropping points) of several natural fats are shown in Table 4.10. Note the correlation between iodine values and melting point, where lower iodine values indicate higher melting points. Also, melting point is what distinguishes fats from oils. In a general sense, oils have melting points below room temperature (note that room temperature varies in different regions around the world) and are liquid, whereas fats have some solid fat content at room temperature and are solid or semi-solid.

Final melting point values are highly significant in confectionery fats for numerous reasons. Mouth temperature is typically a few degrees below body temperature, perhaps around 34–35 °C (93–95 °F). Any fat that has a higher final melting temperature will not melt in the mouth, it must be chewed, resulting in a waxy mouthfeel with reduced flavor notes. For this reason most fats used in confections need to have melting points of 35 °C (95 °F) or less to entirely melt in the mouth. On the other hand, the fats must be sufficiently solid that they do not melt at ambient conditions. In warm environments, where temperatures may exceed 35–40 °C (95–104 °F) on a regular basis, higher melting point fats may be desired. This is particularly true of compound coatings as discussed in Chapter 16.

4.3.2.2 Melting Characteristics

Since natural fats are made up of numerous components, they exhibit a melting range (or a melting profile) rather than a specific melting point. That is, natural fats exhibit increasing amounts of crystalline (solid) fat as temperature is decreased as additional TAG species crystallize. Conversely, as temperature increases, more and more TAG melt so the amount of solid fat decreases. The nature of this melting profile is an important physical property of fats in confections and is often controlled through fat modification technologies to give desirable attributes.

4.3.2.2.1 Solid Fat Curves

Historically, the relative amount of solid fat at any temperature has been measured by the extent of volume expansion of a fat in a technique called dilatometry. Since fat crystals have smaller volume (are more dense) than liquid fat, the relative amount of crystallized fat at any temperature can be measured by quantifying the change in volume of a fat sample. Dilatometry was traditionally done in capillary tubes, but the process of equilibrating multiple fat samples at different temperatures was very time consuming. The volume change at any temperature was compared to the maximum volume change to give a relative amount of solid fat. However, since even at very low temperatures, natural fats are not all solid (there is always some liquid fat remaining), the values obtained with dilatometry are not true solid fat levels, but only relative values. Thus, when dilatometry is used to measure solid fat, it is labeled solid fat index (or SFI), indicating that is not the "true" solid fat content at each temperature. With the advent of more rapid and more accurate methods of measuring solid fat, dilatometry is now an outdated method, although SFI may still be used at times to characterize natural fats.

More common for measurement of solid fat is pulsed, time-domain nuclear magnetic resonance (TD-NMR), which gives the relative amounts of solid and liquid fat at any temperature. In this method, a radio frequency pulse is applied to a sample of fat and the relaxation, or decay, of atomic spins is measured over time. The excitation and decay of atomic spin in a molecule is related to its state, with molecules in crystalline state relaxing more quickly than molecules in the liquid state. These differences in decay patterns are used to measure (or calculate) the amount of solid fat in a sample at any temperature. Although there are numerous limitations to the measurement (Timms 2003), with appropriate calibration and careful operation, pulsed NMR can be a very simple and quick method of estimating solid fat content (SFC) at any temperature. This of course assumes that the sample has completed crystallization, so that liquid and crystalline states in the sample are in equilibrium.

To ensure equilibrium crystallization for SFC determination, fats must be tempered, or treated with an appropriate time-temperature profile, to make sure they have fully crystallized into the most stable polymorph at the measurement temperature. For fats that exhibit complex polymorphism, this requires an extensive (40–60 h) hold at a temperature (19–26 °C) that ensures complete crystallization to the equilibrium SFC. However, as Timms (2003) points out, crystallization of fats to complete equilibrium may take days and even weeks.

Figure 4.5 shows SFC curves for several natural fats and the resulting melting profiles. Milk fat, because of the wide variety of TAG components, has relatively low SFC at 0 °C and melts gradually until there is no crystalline structure between 35 and 40 °C. The lower SFC means butter is softer than cocoa butter at low temperatures. Cocoa butter is a relatively simple fat in terms of molecular composition and exhibits a rather sharp melting profile. Cocoa butter has about 80–90% solid fat at 0 °C, still has over 70–80% solid fat at room temperature, and then is completely melted between 34 and 37 °C (93–99 °F). In Figure 4.5 it can be seen that palm kernel and coconut oils fall somewhere between milk fat and cocoa butter in melting properties.

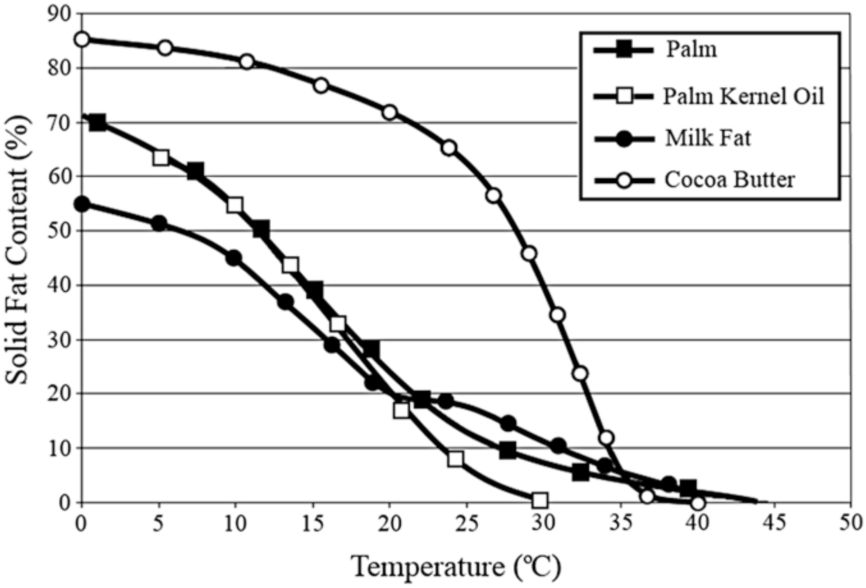


Figure 4.5 Typical solid fat content (*SFC*) curves for milk fat, cocoa butter, palm oil and palm kernel oil

SFC curves are very important quality indicators for fats used in confections, particularly in terms of flavor release and mouth feel. To a first approximation, hardness of a fat is correlated directly with SFC. It is the high SFC of cocoa butter that gives solidified chocolate its characteristic snap. Other vegetables fats may be modified in some way (see Section 4.5) in order to create a similar SFC curve as cocoa butter. Besides SFC, other properties (i.e., flavor, oxidative stability, etc.) are also important for determining the application of a particular fat in a confectionery application.

4.3.2.2.2 Calorimetry

Calorimetry has also been used to characterize the melting (and crystallization) behavior of fats. If a fat is cooled under controlled conditions, the temperature changes during solidification indicate exothermic (or even endothermic) events. Fats that crystallize more quickly have a more rapid onset of temperature increase (due to the exothermic crystallization event) and a higher plateau temperature than those fats that crystallize more slowly and to a lesser extent. Such curves, as measured by the so-called Jensen or Shukoff cooling curves (Timms 2003), were often used in the past (and sometimes still today) to indicate crystallization behavior of fats.

More commonly, a differential scanning calorimeter (DSC) is used to document the changes in enthalpy associated with either crystallization (cooling) or melting (heating) as the temperature of a fat sample is changed. When fat melts, heat is removed from the environment, giving a cooling effect (endothermic). In a DSC, a small sample of fat is contained in a sample pan exposed to a carefully controlled thermal profile. An empty pan is used as a reference to indicate the changes in enthalpy associated with the fat sample. When a solidified fat is heated, the endothermic heat flux associated with melting fat is measured by the DSC, which gives a characteristic melting pattern indicative of the particular fat. In the same way, as a liquid fat is cooled, it eventually reaches a point where it crystallizes, releasing latent heat of fusion, which is detected as a crystallization exotherm (gives up heat) in the DSC. The temperature and relative extent of release of latent heat, as well as the nature of the peaks generated, are characteristic of the type of fat being crystallized. In particular, the molecular composition and the polymorphic crystallization behavior determine the nature of the peaks observed with DSC.

DSC scans themselves are not sufficient to distinguish the different polymorphs of a fat unless the different polymorphic forms have been previously identified by x-ray analysis. For example, milk fat exhibits three different peaks upon melting (Figure 4.6) even though x-ray spectroscopy shows that only the β′ polymorph exists. This melting behavior is attributed to three different classes of TAG that melt together (Timms 1980; Hartel and Kaylegian 2001). The low melting component, approximately 70% of the mass, is made up of TAG containing one long-chain, saturated and two short-chain or unsaturated fatty acids. These short-chain and unsaturated TAG have low melting point, less than about 15 °C (59 °F). The middle-melting component, making up about 25% of the mass, contains TAG with two long-chain saturated fatty acids and one short-chain or unsaturated fatty acid. The melting point of this fraction is about 35–40 °C (95–104 °F). The high-melting component, making up only about 5% of the mass, contains all long-chain fatty acids and has a melting point, when separated from the rest of milk fat, of about 50 °C (122 °F). It is the complex molecular composition of milk fat that leads to this behavior.

In contrast, when liquid cocoa butter is cooled and then immediately reheated, two melting peaks are seen (Figure 4.7). As confirmed by x-ray spectroscopy, the first peak, between 15 and 28 °C, is due to melting of the β′ polymorph, whereas the second peak, with peak temperature between 30 and 35 °C, is due to melting of the β polymorph, as compared to the single peak (the β

Figure 4.6 Melting curves for milk fat from differential scanning calorimetry (With permission from Hartel 2001)

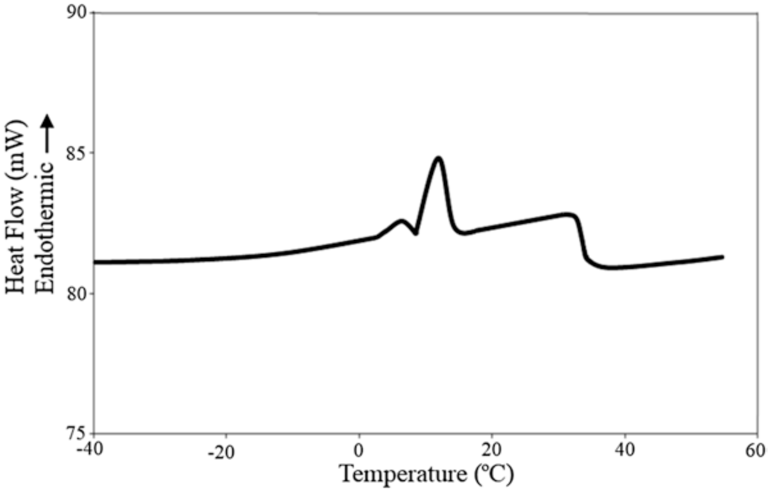
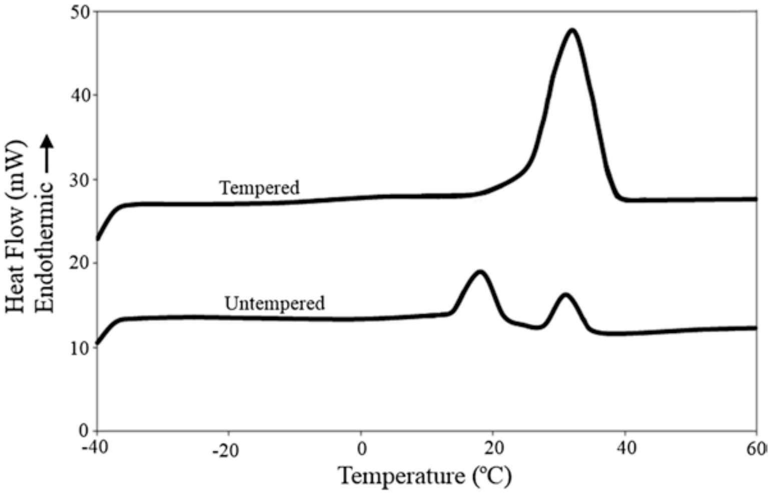


Figure 4.7 Melting curve for tempered and untempered cocoa butter from differential scanning calorimetry (With permission from Hartel 2001)



polymorph) for tempered chocolate. The relatively simple molecular composition of cocoa butter leads to formation initially of the β′ polymorph, followed by transformation to the β polymorph. The exact locations of these peaks may vary slightly for cocoa butters from different origins, due primarily to slight differences in chemical composition (see Section 15.5.4).

4.3.2.3 Phase Diagrams

Thermodynamic principles govern the phase behavior of lipids. The equilibrium phase at any temperature is the one with lowest Gibbs free energy. Figure 4.8 shows a generic schematic diagram of the Gibbs free energy of the liquid phase and different polymorphs of a pure TAG. The most stable polymorph, the β form, has the lowest Gibbs free energy, whereas the less stable forms have sequentially higher free energy.

However, all natural fats used in confectionery contain numerous different TAG and the phase behavior of the mixture is determined by the interactions among individual TAGs. Various studies have delved into the phase behavior of specific binary mixtures of TAG to the extent that the specific phase behavior can be predicted for certain types of mixtures (Timms 2003; Himawan et al. 2006). Timms (2003) describes four different types of phase diagrams for binary mixtures of fats.

1. *Monotectic continuous solid solution*. Occur for mixtures of TAG that are similar in melting temperature, molar volume and polymorphism. The mixture forms a solid solution defined by liquidus and solidus lines. Examples: SSS + SSE, POS + SOS (Figure 4.9a).
2. *Eutectic*. Occurs in mixtures of TAG that are different in molar volume, shape, and polymorphism, but similar in melting point, with limited mutual solubility. The mixture has a liquidus line with a minimum temperature at the eutectic point and, in principle, a solid forms with specific composition of the two components (a eutectic solid). Examples: PPP + SSS, POS + POP, SOS + SOO (Figure 4.9b).
3. *Monotectic partial solid solution*. Occurs in mixtures of TAG with widely different melting point. The mixture has continuous liquidus line, but shows two solid forms. Example: PPP + POP.
4. *Molecular compound/double eutectic*. Occurs in TAG that form a molecular compound at some intermediate concentration, giving two eutectic points, one on each side of the molecular compound.

Of these four binary phase diagrams, the first two are by far the most important in mixtures of TAG's important in confectionery fats.

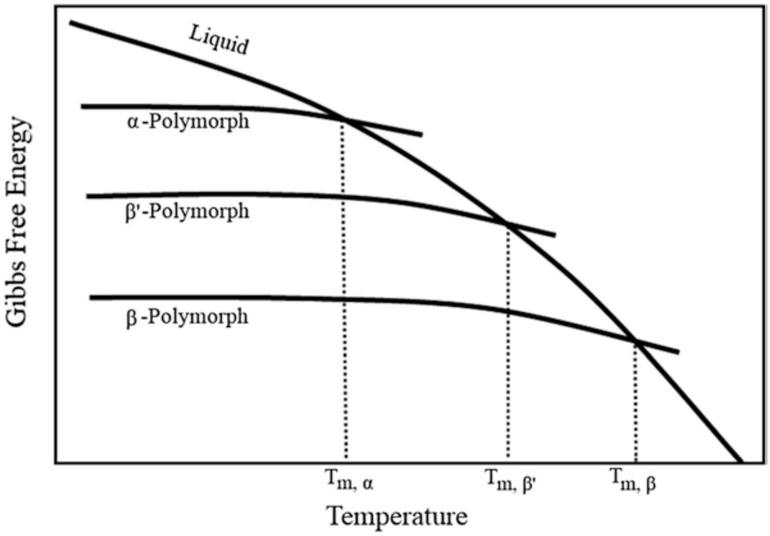


Figure 4.8 Schematic Gibbs free energy diagram for a pure triacylglycerol

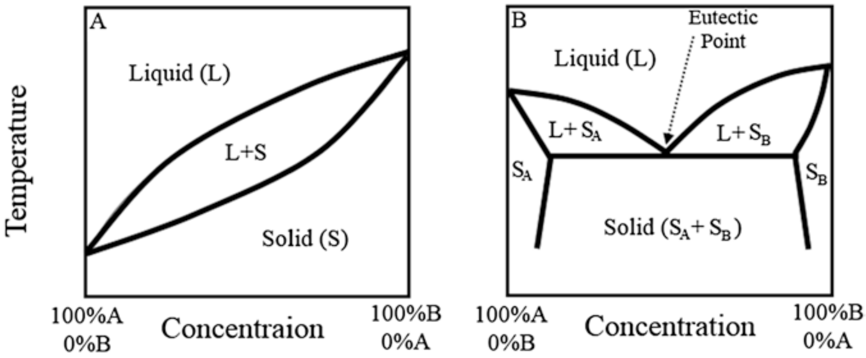


Figure 4.9 Schematic of common phase diagrams for binary mixtures of fats. (**a**) continuous solid solution and (**b**) eutectic phase diagram

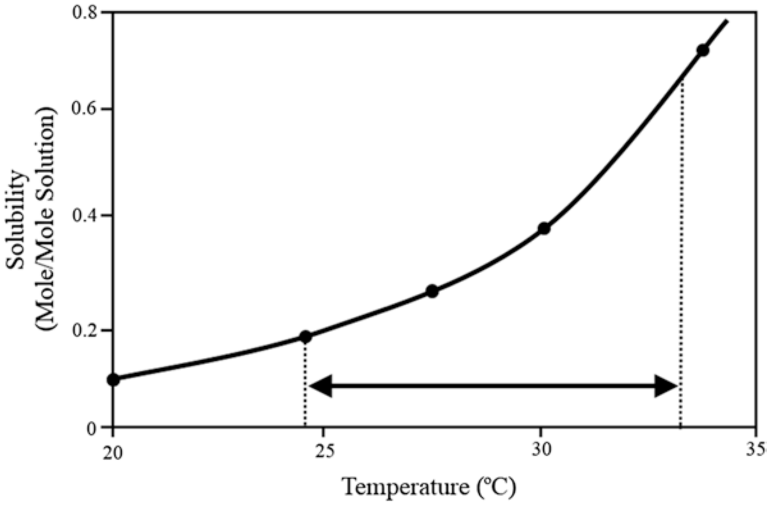


Figure 4.10 Solubility of monounsatured triacylglycerols from cocoa butter in canola oil (Liang and Hartel, unpublished)

Another way to look at phase behavior of certain TAG is through a solubility curve. Certain TAG with very high melting point (e.g., tristearin) may dissolve in a very low melting point oil (e.g., triolein), in the same way as solute dissolves in solvent (e.g., sucrose in water). For example, the solubility of tristearin in triolein was measured to vary from 0.2% at 42.2 °C (108 °F) to 16.1% at 61.9 °C (143.4 °F) (Ward et al. 1955). Although this is a very simple case of two TAG with widely different melting point, the general principle of high-melting fats dissolving to some extent in liquid oils applies throughout natural fats.

As noted before, natural fats are comprised of numerous, sometimes hundreds, of TAG, so simple binary mixture phase diagrams are insufficient to understand the phase behavior of natural fats. Although attempts have been made to use thermodynamic principles to detail phase behavior of complex mixtures of fats, as summarized recently by Himawan et al. (2006), these have met with limited success. Empirical approaches are still used to describe phase behavior of natural fats. An empirical example is the measurement of the solubility of the cocoa butter monounsaturated TAG (SOS, POP, POS) in a liquid oil, in this case canola oil, as shown in Figure 4.10. In principle, this behavior occurs in all natural fats where both very high melting TAGs mix with very low melting TAGs (Zhou and Hartel 2006). Natural fats exhibit complex phase behavior and using a single final melting

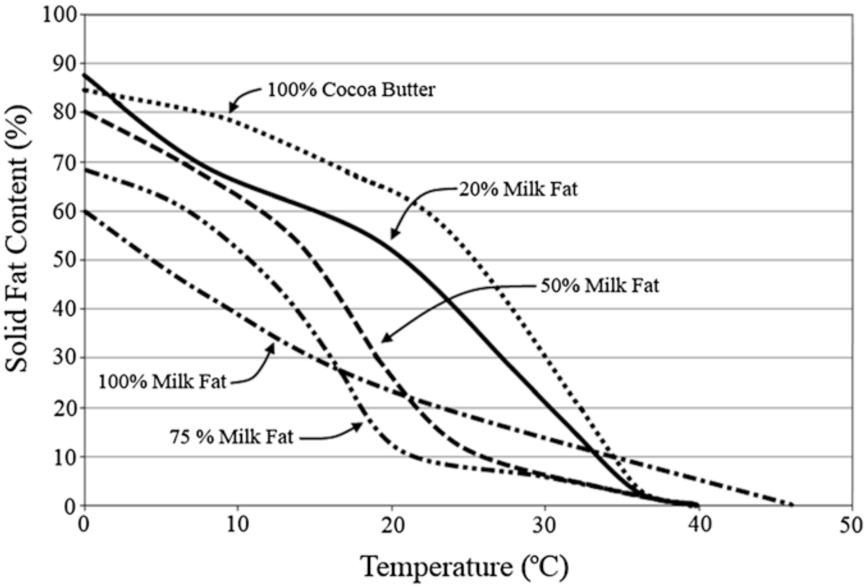


Figure 4.11 Solid fat content (*SFC*) curves for mixtures of milk fat and cocoa butter (With permission from Hartel 2001)

point to describe this phase behavior grossly simplifies the situation.

Another empirical approach for describing the phase behavior of complex fats, described by Timms (2003), applies to binary mixtures of different fats. In this form, phase diagrams similar to those in Figure 4.9 are obtained, but with a few key differences. The mixture of a wide array of TAG means there is no single melting point (rather, there is a range of melting temperatures) and this means that the liquidus and solidus lines do not meet. Also, the eutectic point for mixtures of fats becomes less precise than for a simple binary mixture. For these reasons, the application of these "pseudo-phase diagrams" has not become wide-spread in the confectionery industry.

Often, the eutectic behavior of a binary mixture of fats is important since this leads to either undesired softening (milk fat and cocoa butter in milk chocolate) or intentional softening (coconut oil and cocoa butter in ice cream coatings or chocolate melt-aways). This eutectic behavior can be seen, for example, in the SFC curves for milk fat and cocoa butter at different mixture ratios, as seen in Figure 4.11. Mixtures of milk fat and cocoa butter have melting profiles depending on the ratio of the two fats. Addition of 20% milk fat to cocoa butter (as might be found in a milk chocolate) results in a significant reduction in SFC (up to 18% at 20 °C (68 °F)), causing significant softening of the mixture compared to the initial cocoa butter. This effect of milk fat on cocoa butter is why milk chocolate is typically softer and has less snap than a dark chocolate. When 50% milk fat is added to cocoa butter, the resultant mixture has a melting profile that drops below even the melting profile of the milk fat itself. This behavior, where the mixture has lower SFC than either of the two component fats, demonstrates the eutectic mixing effect between milk fat and cocoa butter. At higher levels of milk fat, the effect is even more significant. These SFC curves can be reconstructed to better document the mixing behavior of the two fats, in the form of isosolid diagrams.

4.3.2.3.1 Isosolids (or Isotemperature) Diagrams

To document the mixing behavior of two fats, the isosolids diagram is often used (Timms 1979; Bigalli 1988). In this case, the solid fat content curves of mixtures of two fats, as seen in

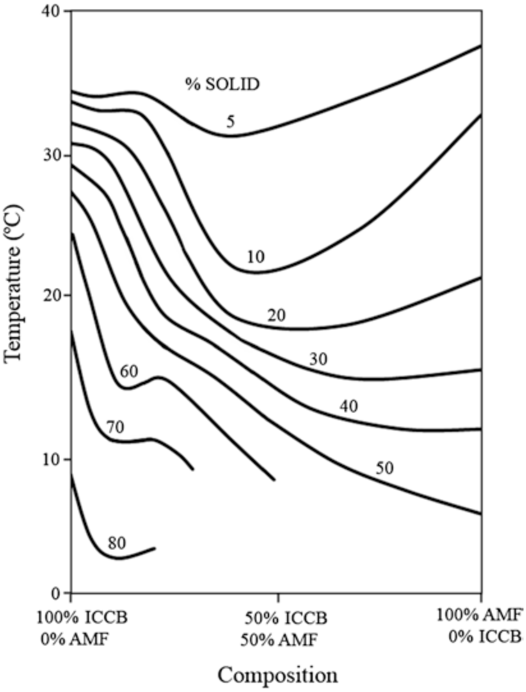


Figure 4.12 Isosolid diagram for mixtures of anhydrous milk fat (*AMF*) and cocoa butter (*ICCB*) (With permission from Hartel 2001)

Figure 4.11, are replotted to show either lines of constant SFC at different temperatures or lines of constant temperature at different SFC. The isosolids diagram for milk fat and cocoa butter are shown in Figure 4.12. The eutectic phase behavior is clearly seen as the reduction in temperature (the dip in the curves) for a given SFC at mixtures of milk fat and cocoa butter between about 30% and 70% milk fat.

Figure 4.13 shows schematically the range of mixing behaviors of two fats when plotted on an isosolids diagram. When two fats are completely compatible and have the same melting point, the lines indicating constant solid fat content are straight and horizontal, as seen in Figure 4.13a. This behavior is exhibited when cocoa butter is mixed with cocoa butter equivalents (CBE) (see Chapter 16). When two fats are essentially compatible but have very different melting points, the level of solid fat decreases linearly with the level of addition of the fat with lower melting point (Figure 4.13c). This occurs, for example, when peanut oil and cocoa butter mix together. As the level of peanut oil increases, the amount of solid

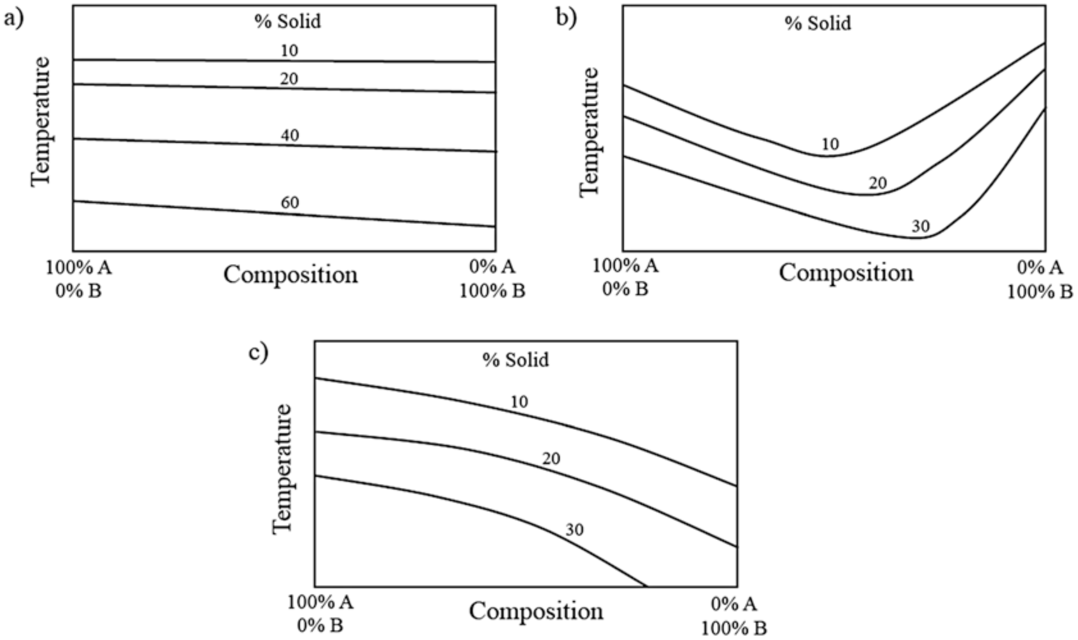


Figure 4.13 Isosolid diagrams (highly schematic) for mixtures of two fats: **a** two fully compatible fats; **b** fats showing eutectic mixing behavior; **c** fats showing dilutional softening behavior (With permission from Hartel 2001)

fat decreases linearly. When two fats are incompatible, but have similar melting temperatures, eutectic behavior is often observed, where the mixture has a decreased SFC below that of each individual fat (Figure 4.13b). In this case, the molecules of one fat impede crystal formation of the other fat. The example of milk fat and cocoa butter in Figure 4.12 indicates eutectic mixing behavior between the TAG of these fats.

4.4 Crystallization of Fats

Although phase behavior governs the thermodynamic aspects of crystallization and dictates the final equilibrium state, kinetic factors often have a significant effect on how and when natural fats crystallize. Kinetic factors include the ability of heat and mass to move through and within a system. Of importance in fat crystallization are such parameters as heat transfer rates, mass transfer rates (diffusion, stirring), and molecular mobility.

When fats are cooled below their melting point, the TAG form into a crystalline lattice where the molecules are organized in a uniform pattern to minimize their free energy. Due to the mixture of TAG molecules in natural fats and the complex phase behavior that exists because of that variety, crystallization of lipids has proven difficult to deal with theoretically and is most often treated empirically (Hartel 2001; Himawan et al. 2006). However, the general steps of crystallization, as covered for sugars in Chapter 2, also apply to fats. That is, nucleation first occurs as molecules transform from liquid to solid, followed by crystal growth, which continues until phase equilibrium is reached. Subsequent changes in the crystalline structure occur due to Ostwald ripening, polymorphic transformations and phase separation as the crystalline structures seek to minimize free energy.

4.4.1 Nucleation

In the liquid state, lipid molecules are relatively free to move around and have relatively high free energy. In the crystal lattice, on the other hand, each molecule associates on each side with the neighboring molecules, which greatly restricts the ability of molecules to move around. Thus, molecules in the crystalline state have much lower free energy than molecules in the liquid state. Upon crystallization, the difference in energy between liquid and crystalline molecules is given up as the lattice is formed and heat is released as latent heat (or heat of fusion). This heat of fusion (also sometimes called heat of crystallization) must be removed from the vicinity of the crystal for crystallization to continue. If not, the temperature around the crystal goes up (due to release of latent heat) and further crystallization slows down. The importance of this concept is shown in the practice of chocolate tempering and cooling as noted in Section 15.4.12.

As temperature decreases, TAG molecules form lamellar structures that eventually become crystal nuclei, as depicted schematically in Figure 4.14. Nucleation is enhanced as the temperature is lowered, with the driving force for nucleation being the temperature differential with the melting point of the fat. As noted previously, natural fats do not have a distinct melting point, but rather show a melting range. Furthermore, each polymorph has its own melting point, further complicating any quantitative thermodynamic expression of temperature driving force. Still, in many cases, the final melting point of the most stable polymorph is often used as the base to characterize temperature driving force for crystallization.

The polymorph that forms first and the rate of nucleation depend on various factors, including the nature of the TAG present, the presence of high-melting minor impurities (e.g., phospholipids), temperature, cooling rate, and agitation rate or shearing (or, more broadly, external energy input). As noted earlier, lipids exhibit monotropic polymorphism, meaning that lower stability polymorphs form first, followed by polymorphic transformation to more stable forms. Despite the fact that more stable polymorphs have a greater nucleation driving force (temperature differential), more unstable polymorphs nucleate first due to the differences in energy barrier for formation

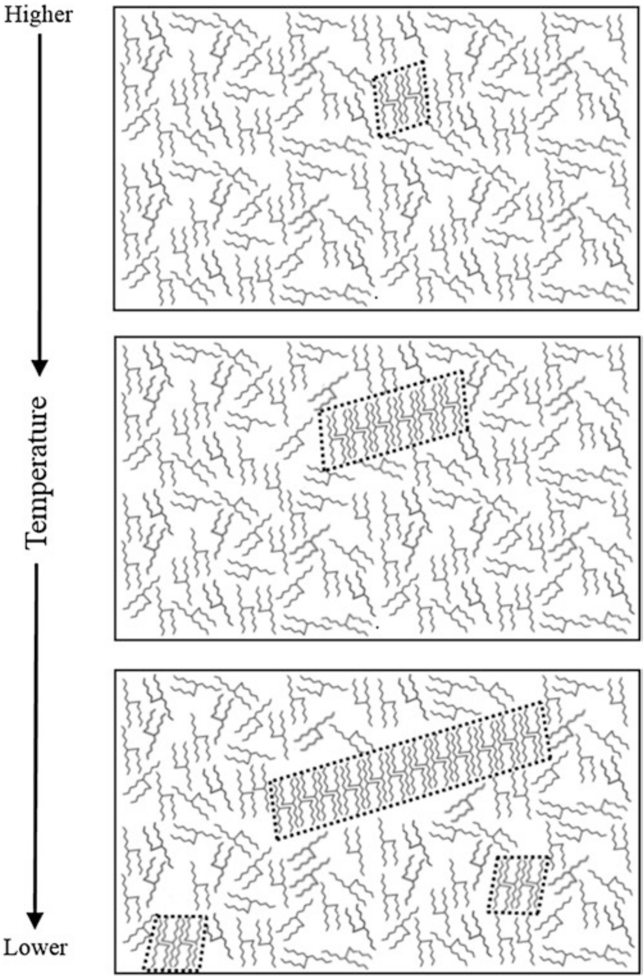


Figure 4.14 Schematic depiction of triacylgycerol association as nucleation occurs with a lowering of temperature

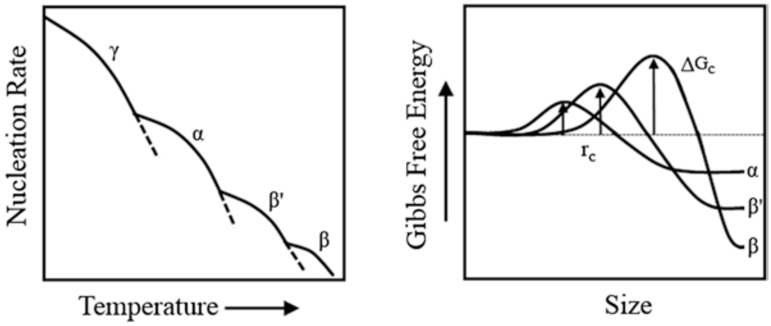


Figure 4.15 Schematic depiction of nucleation rate and free energy change for nucleation of lipid polymorphs (With permission from Hartel 2001)

of the different polymorphs, as shown schematically in Figure 4.15. The rate of nucleation, or number of nuclei formed per unit volume per time, is much higher for α and β′ polymorphs compared to the most stable β polymorph. Even though temperature driving force (temperature differential below the melting point) and the free energy values of the less stable polymorphs are greater than for the more stable polymorphic forms, the less stable polymorph forms preferentially and at a higher nucleation rate due to the lower energy barrier that needs to be overcome to form the lattice structure. This lower energy barrier for nucleation is generally attributed to a lower interfacial tension between crystal and liquid melt. In general, nucleation of lipids occurs in either the α or β′ form due to the very low nucleation rate of the most stable β polymorph.

In natural fats, the lower the temperature, the greater number of TAGs that can participate in forming the crystal lattice. As temperature goes down, more TAG molecules become available for orientation into the crystal lattice and the solid fat content increases as temperature decreases. Because of the complex mixture of TAG, lipids form mixed crystals, with additional TAG incorporating into the lattice as temperature is lowered. The rate of cooling also affects nucleation rate, the polymorph that forms first and the specific type of TAG that are incorporated into the mixed crystal lattice. In general, faster cooling means TAG molecules have less time to diffuse away from the lattice and a more diverse set of TAG become incorporated into the lattice compared to slow cooling. When fats are cooled quickly, the onset of nucleation occurs at a lower temperature (than for slow cooling), there are more diverse TAG's incorporated into the mixed crystals, and the SFC is higher (than for slow cooling). In slow cooling, TAG molecules have more time to diffuse in the liquid phase and those molecules with a lower melting point (e.g., those containing shorter chain and more unsaturated fatty acids) have more time to diffuse away from the lattice. The result is crystals with purer TAG composition and lower SFC compared to rapid cooling.

Another parameter that significantly affects lipid nucleation is external energy input, whether agitation or shearing rate from a stirrer or an external energy source (e.g., ultrasound). As with sugars and other materials (see Chapter 2), stirring or other energy input allows the molecules to come together more readily to form a crystal lattice. That is, higher agitation rates generally lead to greater nucleation rates. Along the same line, nucleation in a shear field occurs at a higher temperature than nucleation during static cooling. In the case of lipids, intense shearing has also been shown to affect the polymorphic form, with more stable polymorphs evident under intense shearing action, although there is not universal agreement on the mechanisms by which shear forces affect lipid crystal formation (Sato 2001).

The rate of crystal nucleation also affects crystal shape and size, which may have significant impact on the physical properties of fats and fat-based products. In general, numerous small crystals are desired in most food applications (Hartel 2001). This comes from nucleating at conditions that give the highest possible nucleation rate (i.e., lower temperatures and more shear). Crystal shape also depends on the polymorphic form, with the β′ form typically found in the form of spherulites, or densely-packed, needle arrangements, whereas the β polymorphic forms are more plate-like and may be stacked in multi-layers (Hicklin et al. 1985). The arrangement and interaction of crystals in a food matrix, as well as their size and shape, influences the physical/mechanical properties of the product. Numerous small particles packed tightly together in a fat crystal network, as found in chocolates or coatings, provide hardness and snap, give a glossy appearance, and limit liquid oil migration during storage.

Addition of two natural fats together can also affect nucleation kinetics. A classic example is the effect of milk fat on cocoa butter nucleation (Hogenbirk 1990; Metin and Hartel 1998). The ability of cocoa butter TAG to come together to form nuclei is inhibited by the presence of the milk fat TAG. To counteract this inhibition effect for example in milk chocolate (see Section 15.5.5), lower temperatures are used to promote more rapid nucleation.

The minor impurities found in natural fats (see Section 4.2.1.3) and emulsifiers added to product formulations can also affect nucleation (Smith et al. 2011); however, the results of previous work are somewhat contradictory. Numerous studies have shown that removing the impurities (nonTAG components) in natural fats causes a significant decrease in nucleation rate. For example, crystallization of purified milk fat TAG was faster than the original milk fat with the minor lipids still intact (Herrera et al. 1999).

However, other studies have shown that phospholipids have a significant effect on promoting cocoa butter nucleation (Davis and Dimick 1989). In general, it is thought that if an impurity crystallizes at a higher temperature than the highest melting point TAG, the seed crystals will form a template and promote TAG crystallization. If the impurity remains in the liquid state when crystallization begins, it often acts as an inhibitor to nucleation.

4.4.1.1 Seeding

At times, nucleation of lipids is bypassed through addition of seed crystals that initiate crystallization of the remaining fat. Often, seeds are comprised of the crystallizing material itself, as in seed tempering of chocolate through addition of crystals of the proper polymorphic form of cocoa butter. However, some seed crystals may be a different composition than the fat being seeded, with the seed crystals providing a template for the subsequent crystallization of the remaining liquid fat. For example, fully hardened vegetable (palm) oil may be used as nucleator for palm kernel oil in compound coatings (see Section 16.4). Despite the difference in TAG molecular makeup (lauric versus nonlauric fatty acids), the hardened vegetable oil is thought to help promote crystallization of palm kernel oil. Similarly, the addition of the monounsaturated TAG, BOB (where B is behenic acid and O is oleic acid), has been shown effective at promoting crystallization of cocoa butter, made up primarily of SOS, POP and POS.

In general, there are three requirements for seeds to be effective. First, there must be a polymorphic match in which the seeds must have the same polymorphic structure as the desired form in the crystallizing fat. Second, there should be a match between the aliphatic chains of the seed and the crystallizing fat. That is, chain length differences should be less than four carbon atoms and the seeds should exhibit similar saturation/unsaturation as the TAG of the crystallizing fat. Finally, the melting point of the seed crystals must be significantly above the melting point of the crystallizing fat so that seeds can be added in solid form to the liquid fat.

4.4.2 Growth

In order for nuclei to grow, TAGs from the liquid phase must diffuse through the melt, orient themselves at the interface (crystal/melt), and then incorporate into the lattice structure (Hartel 2001; Walstra et al. 2001). Once a molecule becomes incorporated, there is a release of latent heat, which must be removed in order to maintain the driving force for growth. Any of these steps may be rate-limiting. Since melting of crystalline fats is so much faster than crystal growth rates, it is generally assumed that growth of fat crystals is governed by surface incorporation phenomena (Himawan et al. 2006). That is, the rate of growth is limited by the ability of TAG molecules to orient themselves in the proper three-dimensional conformation and become incorporated into the lattice. Synchrotron x-ray spectroscopy studies have shown that the TAG first stack in a lamellar arrangement before being incorporated into the crystal subcell (Ueno et al. 1999).

In one sense, the rate of growth of lipid crystals is directly related to the mixture of TAG found in natural fats. The presence of TAG with fatty acids of different chain length and degree of unsaturation increase the difficulty of TAG molecules becoming incorporated into the crystal lattice. However, the general similarity of TAG molecules also leads to incorporation of different TAG as a crystal nucleates and grows. For this reason, compound crystals containing a variety of TAG with different fatty acid compositions are found in lipid crystals. Growth at higher rates (lower temperatures and in less stable polymorphs) enhances the ability of TAG with widely different fatty acid compositions to incorporate together into the crystal lattice. Besides the diversity of TAG in natural fats, the presence of minor lipids can also inhibit growth rate of TAG crystals. Mono- and diglycerides present in natural fats, for example, may associate with TAG already in the crystal lattice and inhibit further incorporation of TAG into the lattice.

Another element that makes lipid crystal growth so complex is stratification. Here, incorporation of different TAG may occur at different times during growth due to depletion in the liquid phase. Initially, the highest melting TAG form into the crystal lattice; once these higher-melting TAG are depleted from the liquid phase, another set of TAG with lower melting point begin to incorporate. This gives a stratified crystal with higher-melting TAG in the interior and lower-melting TAG towards the outside of the crystal. Fortunately, since lipid crystals grown under commercial conditions, with sufficient agitation, tend to be fairly small (microns or less), stratification is generally not a problem. When large fat crystals are grown under static conditions, rings and bands can be observed due (at least in part) to TAG stratification.

Fat crystals in the β′ polymorph typically appear as spherulites, made up of agglomerated single crystals. The growth conditions are generally thought to affect the agglomerates (size, density, etc.) but not the primary particles that make up those aggregates (Martini and Herrera 2002; Acevedo and Marangoni 2015).

4.4.3 Polymorphic Transition

In monotropic polymorphism, unstable forms crystallize first and transform to more stable polymorphs over time. These transformations may either occur through melting and recrystallization (melt-mediated) or by molecular rearrangement within the crystal lattice (solid-mediated). The type of transition depends on the nature of the TAG themselves and the environmental conditions, primarily the temperature. An example of melt-mediated polymorphic transition is tempering of chocolate (see Section 15.5.5), where first the fat is cooled well below the melting point of the β′ polymorph to promote nucleation followed by an increase in temperature to a point above the melting point of the β′ polymorph. This causes melting of the unstable β′ form and nucleation/crystallization of the more stable β polymorph. Probably both modes of polymorphic transformation occur under most commercial conditions. Research using high intensity synchrotron x-ray diffraction studies now allows clear determination of polymorphic transformations in lipid systems in real time. However, these studies are still generally limited to static conditions, with no agitation or shearing, so do not always correlate to commercial conditions.

Various factors influence the rate of polymorphic transition, including the processing conditions (shear/agitation, temperature, etc.) and the composition of the fat (TAG profile, minor lipid composition, emulsifiers, etc.). In particular, emulsifiers have been shown to influence the rate of polymorphic transformation (Garti and Yano 2001); however, the effects of emulsifiers are not clearly defined. In some cases, emulsifiers inhibit the rate of polymorphic transformation, probably due to their interactions either within or at the surface of the crystal. In other cases, however, it seems that emulsifiers actually enhance the rate of polymorphic transformation, although the mechanism for this acceleration is unclear. Smith et al. (2011) summarize recent knowledge on effects of impurities on lipid crystallization.

4.5 Modification Technologies

Oftentimes, natural fats do not have exactly the right physico-chemical characteristics needed for a certain confectionery application. For example, the melting profile of palm kernel oil (PKO) is not quite satisfactory for use as a cocoa butter substitute; it is too soft at low temperatures and melts at too low a temperature. Thus, modification and/or fat blending techniques are employed to change the chemical make-up of the fat and thereby change its physical properties to make it appropriate for a confectionery application (see Chapter 16 for more on applications of modified fats in compound coating applications). Three modification technologies are most common for changing the nature of fats; hydrogenation, fractionation and interesterification. Each method has advantages and disadvantages, including the costs associated with each processing technology. Generally, the more complex the process for modification, the higher the cost, although more highly modified fats may also have the most desirable attributes for a specific application. Additional details on modification technologies can be found in Bockisch (1998) and O'Brien (1998).

4.5.1 Hydrogenation

Many natural fats contain unsaturated fatty acids, with melting points lower than room temperature; these are not appropriate for use in confectionery applications unless modified in some way. Vegetable oils from soybean, cottonseed, and corn, for example, are liquid at room temperature due to the high content of mono- and polyunsaturated fatty acids. As seen in Table 4.1, liquid oils contain high levels of oleic, linoleic and even linolenic acids. Many semi-solid natural fats, including palm oil, palm kernel oil and coconut oil, also contain substantial amounts of unsaturated fatty acids (Tables 4.6, 4.7, and 4.8). To increase melting point and enhance utility in confections, unsaturated fatty acids can be hydrogenated (adding a hydrogen atom) to increase the level of saturated fats. For example, oleic acid (one unsaturated double bond) can be hydrogenated to give stearic acid (a saturated fatty acid) with a significantly higher melting point. Likewise, linoleic acid (two unsaturated double bonds) can be saturated to give first oleic acid and ultimately stearic acid. The same progression applies for saturation of linolenic acid during hydrogenation. The general scheme, shown schematically in Figure 4.16 , is that linolenic acid is hydrogenated to linoleic acid, which is hydrogenated to oleic acid and then on to stearic acid. Although the rate of hydrogenation is faster for more highly unsaturated fatty acids (linolenic acid reacts 2 times faster than linoleic acid and 40 times faster than oleic acid), hydrogenation of each species occurs simultaneously (just at different rates).

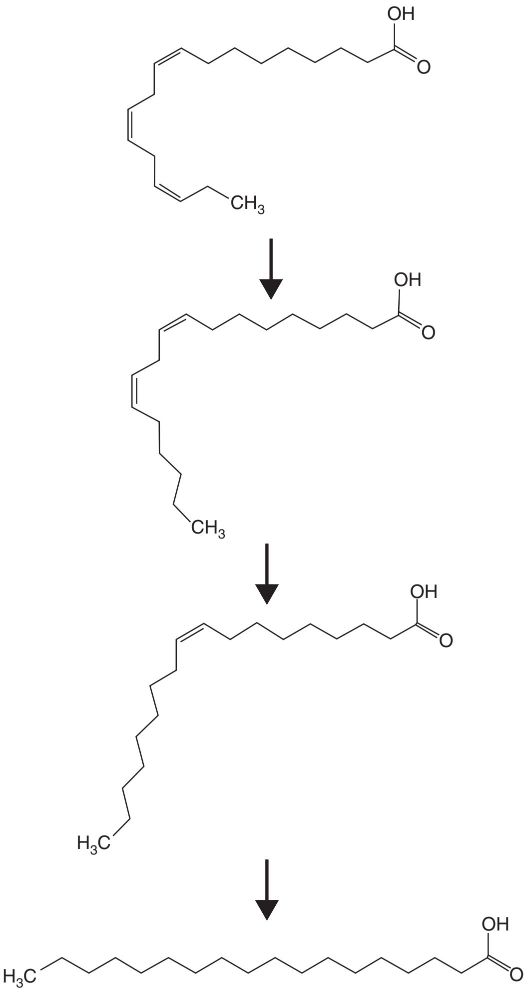


Figure 4.16 General scheme of hydrogenation of polyunsaturated fatty acids (linolenic acid at the *top*) to a fully saturated state (stearic acid at the *bottom*)

Depending on operating conditions, formation of *trans* fatty acids is often promoted during hydrogenation. Chemically, *cis* and *trans* isomers have the same molecular composition but are physically different, as seen in Figure 4.2. The *trans* form of oleic acid (called elaidic acid), with H-atoms on opposite sides of the double bond, has a higher melting point than the *cis* form, which has H-atoms on the same side of the double bond. Because of the bent shape of the *cis* form, the melting point of the most stable form of triolein (OOO) is very low, −2.5 to 5.5 °C (27.5–42 °F), whereas that of trielaidin (EEE) is much higher, 41–42 °C (105.8–107.6 °F), because the *trans* form has a straighter conformation. Conditions in the hydrogenation vessel determine the relative extent of *trans* oleic acid formation. It should be noted that complete hydrogenation, or fully hardening a vegetable oil, results in all stearic acid containing no *trans* fatty acids.

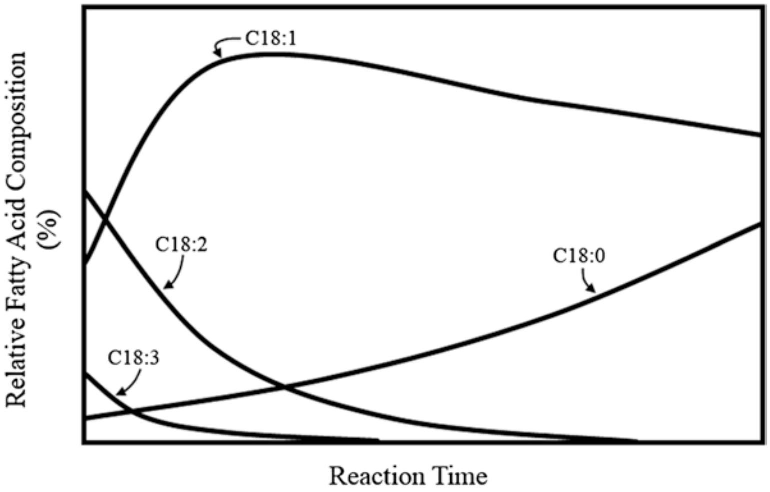


Figure 4.17 General scheme of changing concentration of unsaturated and saturated fatty acids during hydrogenation of a vegetable oil

Hydrogenation is performed by bubbling hydrogen gas through the liquid oil at elevated temperatures and pressures in the presence of a catalyst (e.g., nickel). The rate and chemical products of the process depend on numerous factors. The time the liquid oil spends in the hydrogenation process and the rate of hydrogenation (function of processing conditions) determines the end-point of hydrogenation. The end-point of the process is most often characterized by measuring refractive index, which generally correlates well with iodine value (the ratio of unsaturated to saturated fatty acids). Besides temperature and pressure, the catalyst concentration, type of catalyst, presence of catalyst poisons, and agitation rate are operating parameters that influence the hydrogenation process for a given oil. Of course, the nature of the oil also influences the hydrogenation process. Through control of operating conditions, some specificity in the reaction process is allowed. For example, formation of *trans* fatty acid isomers can be minimized to some extent by choice of reaction conditions.

Often, only partial hydrogenation is needed to modify the melting point of a natural fat to make it suitable for a confectionery application. Due to the production of less unsaturated fats, partial hydrogenation increases both melting point and SFC at any temperature. The general loss and formation of different fatty acids during hydrogenation is shown schematically in Figure 4.17. Linolenic and linoleic acids decrease initially while the oleic acid content increases. At later stages of the process, oleic acid content decreases as more stearic acid is produced. In this simple example, the melting properties of a partially hydrogenated fat depend on the relative composition of unsaturated and saturated fatty acids. Stopping the reaction at any point in time leads to a partially hydrogenated fat with different melting properties due to the relative differences in unsaturated and saturated fats (IV decreases). For example, through partial hydrogenation, the suitability of palm kernel oil for use as a cocoa butter substitute is increased, with the extent of partial hydrogenation determining the SFC at any temperature and the final melting point. More details of modification of fats for use in compound coatings can be found in Chapter 16.

Due to concerns of *trans* fatty acids in the diet and the loss of GRAS status of partially hydrogenated fats, partial hydrogenation of fats to modify the melting profile is being phased out.

4.5.2 Fractionation

Fats with a wide array of TAG molecules can be fractionated, or separated into components with different composition, based on the different properties of those molecules. Specifically, TAG in many natural fats can be separated based on their melting points. The most common methods

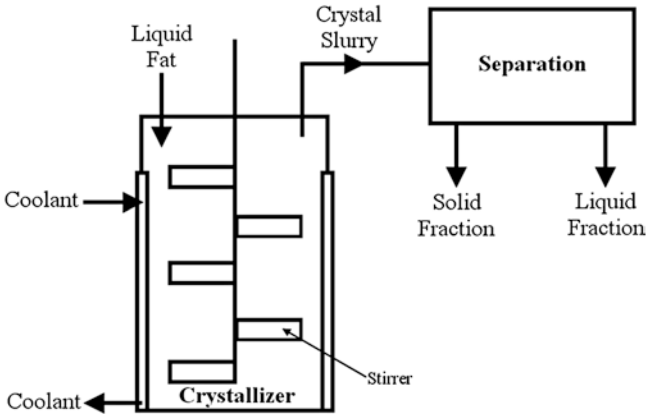


Figure 4.18 Schematic depiction of a melt fractionation process where molten fat is cooled to form a crystal slurry, which is separated to form liquid and solid fractions

for fractionation based on melting point of TAG are dry (or melt) fractionation and solvent fractionation. In fractionation, the molten fat is cooled to controlled temperature, either by itself (dry/melt) or in the presence of a solvent, to promote crystallization of the higher-melting TAG. The crystals are filtered off, leaving a more liquid component depleted in the high-melting TAG. Recently, fractionation of fats in supercritical carbon dioxide has also shown potential for creating unique fat fractions. Other methods of fractionation exist, like separation based on either miscibility of fat crystals in a detergent solution or volatility of different TAG under vacuum; however, these methods are not as widely used for fractionation of confectionery fats.

As shown schematically in Figure 4.18, melted fat is cooled under controlled conditions to partially crystallize the fat to produce a slurry of crystals comprised of high-melting TAG that can be easily filtered from the remainder of the liquid oil (Deffense and Hartel 2003). The filter cake contains the high-melting fraction (sometimes called a stearin because of the concentration effect on stearic acid) of the original fat whereas the liquid oil that passes through the filter is enriched in TAG that contain short-chain and unsaturated fatty acids (sometimes called the olein). The stearin has a melting point significantly higher than the original fat with higher SFC at all temperatures. The low melting fraction may be further processed to produce intermediate fractions and a very low melting point olein. In multi-step fractionation, the first olein produced would be subsequently cooled further to crystallize another set of TAG. A second filtration step results in second stearin and olein fractions with different composition and physical properties. Up to three or even four steps are possible although the feasibility of more than one or two fractionation steps is limited due to increased processing costs and reduced yields.

In dry fractionation, a substantial percentage of liquid fat (30–60%) is retained within the crystals, even under high-pressure filtration (Patience et al. 1999). This retained liquid negatively affects the separation between high and low-melting TAG and the yields of each fraction. To enhance fractionation, a solvent such as acetone or hexane may be added to the molten fat prior to cooling. Although some of the fat dissolves in the solvent and later crystallizes out when temperature is lowered, perhaps a more important aspect of solvent addition is to decrease the viscosity of the slurry. This reduces the amount of liquid entrained in the filter cake and enhances separation, increasing the yield and the melting point of the stearin fraction. Typically, solvent fractionation uses lower temperatures than dry fractionation, but produces fractions with more clearly distinguished TAG. However, a distinct disadvantage of solvent fractionation is that the undesirable solvent must be stripped away from the fat prior to use, which also results in loss of flavors. When deodorized fats are used, this is not a problem.

Compared to the original fat, the stearin fraction has increased melting point and SFC at any temperature. This generally enhances its use in confectionery applications, although fractionation conditions can be modified to produce fractions with different melting profiles. The application of fractionated fats in compound coatings is covered in greater detail in Chapter 16.

4.5.3 Interesterification

In nature, the plant or animal organizes the fatty acid positional arrangement in the TAG according to specific needs (e.g., nutrition of the seedling or infant). In general, fatty acids are not distributed randomly on the glycerol molecules of natural fats, which means that those fats can be modified by rearranging the fatty acid placement on the glycerol backbone. Such a change in the fatty acid orientation in a TAG generally results in modification of physical and melting properties. Interesterification can be done either chemically (by far, the most common) or enzymatically (a more recent development) and can be done by randomizing a single fat or by combining two (or more) fats or a fatty acid stream to provide certain advantages (Rozendaal and Macrae 1997).

Chemical randomization of a fat involves adding sodium methoxide as catalyst (other potential catalysts include sodium ethylate, and sodium methylate) at high temperatures and low pressures. This causes the fatty acids to be stripped from the glycerol molecule and then randomly replaced to produce a new, randomized, distribution of fatty acids on the TAG. A simplified schematic of the random interesterification process can be seen in Figure 4.19. For even a single TAG with three different fatty acids, randomization can result in formation of up to six new TAG with different fatty acid arrangements, along with a variety of mono- and diglycerides. When natural fats with tens to hundreds of unique TAG are randomized, the result is a redistribution of fatty acids and a wide diversity of potential new TAG. Because of this randomization, the categories of TAG change, as seen in Table 4.14.

Interesterification can also be directed to some extent through the removal of one or more reactant products during the reaction to govern the reaction process (Laning 1985). For example, lower molecular weight fatty acids can be removed by distillation to promote preferential formation of longer-chain, higher-melting TAG. Alternatively, the higher-melting TAG can be removed during the process by cooling and fractional crystallization. Interesterification, in both cases, continues in the same randomized manner but with a different set of molecules.

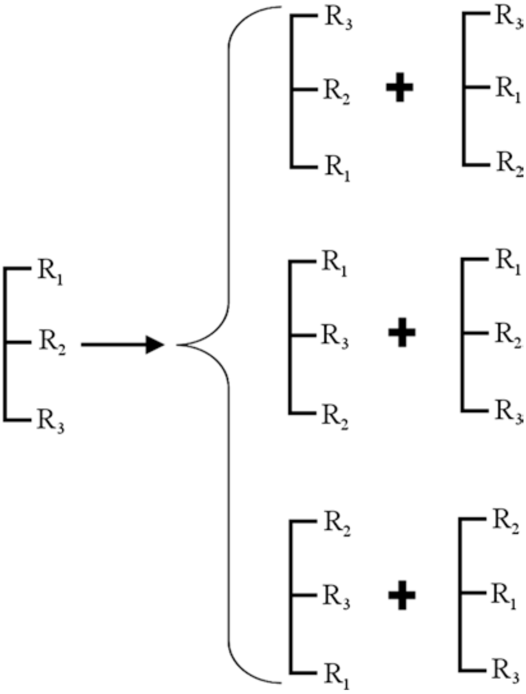


Figure 4.19 Potential random rearrangements of a single TAG with three different fatty acids

In general the chemical randomization of interesterification leads to an increase in the melting point of vegetable fats (see Table 4.14), but a decrease in the melting point of animal fats. List et al. (1997) attributed this to the general positional arrangement of fatty acids on the glycerol, with vegetable fats generally having palmitic and stearic acids in the *sn*-1 and *sn*-3 positions of the glycerol. Interesterification also usually results in an increase in the SFC at high temperatures with a corresponding decrease in SFC at lower temperatures. These changes can make a fat that was previously too soft become suitable for certain applications. However, the flattening of the SFC

Table 4.14 Changes in categories of triacylglycerols (TAG) due to random chemical interesterification

Fat		Dropping point (°C)	SaSaSa[a]	SaSaUn[a]	SaUnUn[a]	UnUnUn[a]
Palm oil	n[b]	–	6	50	38	6
	i[b]	–	13	39	37	11
Soybean oil	n	−0.4	0	6	38	56
	i	7.8	1	8	36	55
Cottonseed oil	n	8.5	<1	18	51	30
	i	16.6	3	18	51	50
Peanut oil	n	8.5	0	11	40	49
	i	13.8	1	10	38	51
Coconut oil	n	24.9	81	12	7	0
	i	27.0	74	24	2	<0.1
Palm kernel oil	n	–	76	15	9	0
	i	–	53	37	9	1

Source: Bockisch (1998)

[a] *Sa* saturated, *Un* unsaturated fatty acid

[b] *n* not interesterified, *i* interesterified

curve associated with interesterification may result in a fat that does not have a sufficiently sharp melting profile for use in some confectionery applications. These changes are related to the specific TAG categories, as shown in Table 4.14. In some cases (i.e., palm), both the trisaturates and triunsaturates increase, whereas in other cases (palm kernel and coconut), there is a decrease in trisaturates and an increase in monounsaturated TAG. Again, these differences are related to the complexity of the fatty acids in the natural fat and their specific (nonrandom) arrangement on the TAG.

For example, cocoa butter contains a high proportion of monounsaturated TAG (SOS, POP, POS), with the oleic acid preferentially found on the *sn*-2 position of the glycerol molecule. When cocoa butter is randomized, the oleic acid now becomes evenly spread across all three carbon atoms of the glycerol (Sanders et al. 2003; Berry 2009), resulting in a product with very different properties. In cocoa butter, the melting point increases after randomization, but the desirable sharp melting profile found in natural cocoa butter is lost, as seen in Figure 4.20.

If a second fat is added prior to randomization, the fatty acids of the second fat are randomly mixed with the fatty acids from the first fat. This also produces a new fat with distinct physico-chemical properties from either of the two initial fats. For example, palm kernel oil (a lauric fat) can be randomized in the presence of palm stearin (high in long-chain saturated fatty acids) to give a fat with a very sharp melting profile, similar to that of cocoa butter, and with a melting point less than 40 °C. Interesterification can also be combined with other forms of fat modification (hydrogenation or fractionation). A wide range of modified fats with nearly any chemical composition and physical functionality can be produced through these combinations and processes.

Another factor that affects melting characteristics of interesterified fats that is often overlooked is the remaining diglyceride (DAG) content. During interesterification, fatty acids are removed from the glycerol and when they are added back again, there is a distinct possibility that not all the glycerol carbons are esterified with fatty acids, leaving free fatty acids (FFA), monoglycerides (MAG) and DAG in the mixture of newly formed TAG. FFA and MAG are mostly removed during the distillation step following interesterification, but DAGs are not removed by distillation. This may cause interesterified fats to have significantly elevated levels of DAG, which can cause a significant effect on both melting properties and physical attributes of the solidified fat (e.g., hardness).

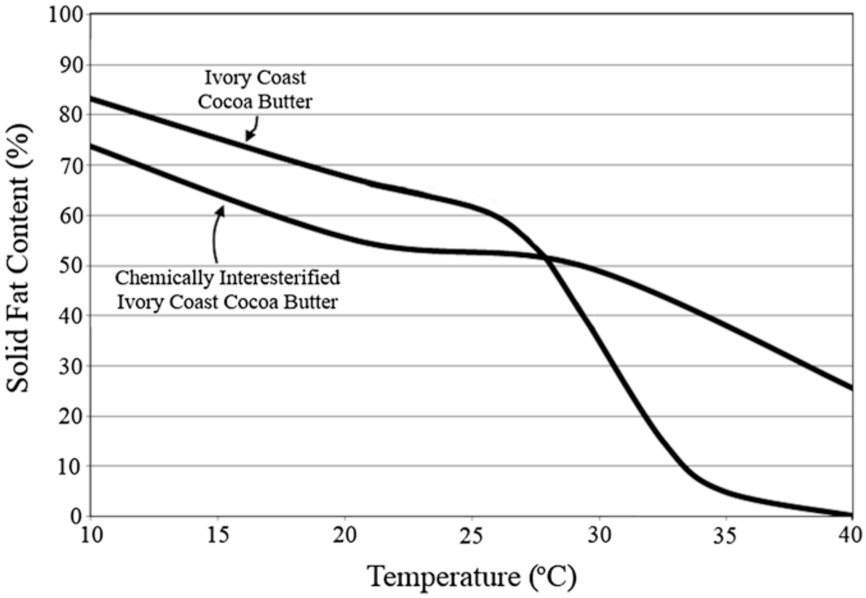


Figure 4.20 Change in melting profile of cocoa butter due to random interesterification

Interesterification can also be accomplished using enzymes rather than through chemical addition. Enzymatic interesterification utilizes lipases to remove the fatty acids from the glycerol and replace them in different sites. One advantage of the enzymatic process is that some level of specificity can be directed into the reaction through choice of lipase. Although many lipases are completely random and will attack any fatty acid in any position on the glycerol, there are certain lipases that are more specific whose actions are directed either by fatty acid type (chain length and/or unsaturation) or placement on the glycerol. With very few exceptions, available lipases are *sn*-1,3 specific, meaning they preferentially remove the fatty acids from the outer carbons of the glycerol molecule leaving the fatty acid on the middle (*sn*-2) position intact. Further direction of the enzymatic interesterification reaction can be accomplished by choice of solvent. For example, Liu et al. (2007) used supercritical CO_2 as the solvent to better direct enzymatic modification of a blend of lard with tristearin to produce a confectionery fat with desirable melting properties.

4.6 Emulsifiers

Emulsifiers, or surface-active agents, are used widely in the confectionery industry because they serve numerous purposes. From promoting emulsification in caramels to reducing viscosity of chocolates, emulsifiers provide substantial benefits in confectionery products and processing technologies. Detailed discussion of emulsifier chemistry and food applications can be found in McClements (2005) and Hasenhuettl and Hartel (2008). Specific discussion of emulsifier application in confections can be found in Weyland and Hartel (2008).

4.6.1 Use of Emulsifiers in Confections

An emulsifier is a molecule that has both hydrophobic (water-repelling or oil-loving, sometimes called lipophilic) and hydrophilic (water-loving) components on the same molecule. As a molecule that can bridge between aqueous and oil phases, an emulsifier can provide stability to two

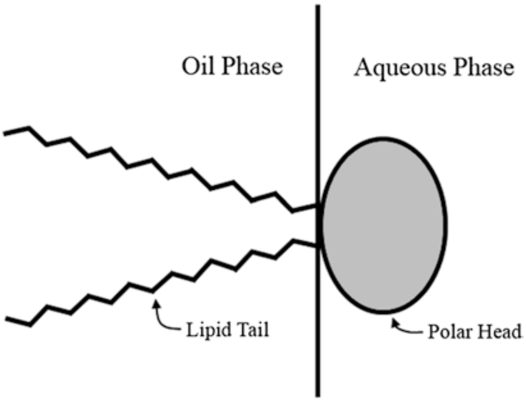


Figure 4.21 Schematic representation or orientation of an emulsifier molecule at an oil-water interface

phases that would not normally mix together. As such, emulsifiers are typically used to help stabilize an emulsion of one phase within another. Emulsions can be either water-in-oil (W/O), where water droplets are dispersed through a continuous oil phase, or oil-in-water (O/W), where oil droplets are dispersed within a continuous aqueous phase. An emulsifier bridges the two phases of the emulsion.

A very simple visualization of an emulsifier molecule is shown in Figure 4.21**.** The hydrophilic portion of the molecule is attracted to the aqueous phase while the lipophilic aspect of the molecule is attracted to the oil phase. Thus, the emulsifier sits at an oil-water interface with the hydrophilic (water-loving) group on the aqueous side and the lipophilic (lipid-loving) group on the oil side of the interface. In so doing, the emulsifier reduces the interfacial tension of the oil-water interface.

The interfacial tension at the boundary between an oil and water phase arises due to the lack of interaction between molecules across the boundary, in the same way that a surface of water exposed to air exhibits a surface tension. The molecules on each side of the interface can only interact with neighbors on their own side of the interface; thus, there is a force on the molecules directly on the interface because they can only interact on three sides. When an emulsifier resides at that boundary, however, it provides molecular interactions across the boundary and reduces the interfacial tension by an amount dependent on the nature and concentration of the emulsifier. At low emulsifier addition levels, interfacial tension decreases as emulsifier concentration increases. Once the interface is completely filled with emulsifier molecules, no further decrease in interfacial tension is seen. This emulsifier level is called the critical micelle concentration (CMC). Further addition of emulsifier molecules results in structure formation (e.g., micelles) within one of the phases (oil or water), depending on the nature of the emulsifier.

The lipophilic component of most emulsifiers is based on a fatty acid group, but these can be saturated, monounsaturated or polyunsaturated. The polar head group, or hydrophilic component, of an emulsifier can take quite varied forms and sizes. It can be as simple as a hydroxyl group or as large as a phosphatidyl-type group (as found in lecithin). Figure 4.22 shows some typical lipophilic and hydrophilic components of food emulsifiers.

Emulsifiers play several important roles in confections (Table 4.15). Besides helping to promote emulsification and stabilization of fats in caramels and toffees, they play a critical role in controlling viscosity in chocolates and coatings. Furthermore, emulsifiers can act as bloom inhibitors in compound coatings. Physically, emulsifiers also help provide lubrication and antisticking during processing and consumption of such confections as caramel, licorice and tableted candies. In gum, emulsifiers help plasticize gum base and promote hydration of the gum bolus during chewing. Emulsifiers also help promote mold release in starchless molding lines.

4.6.2 Emulsifier Types and Characterization

A number of different emulsifiers are used in confections, with the choice depending on the desired functionality. Emulsifiers are characterized according to their properties, primarily on whether they tend to be more water soluble or more lipid

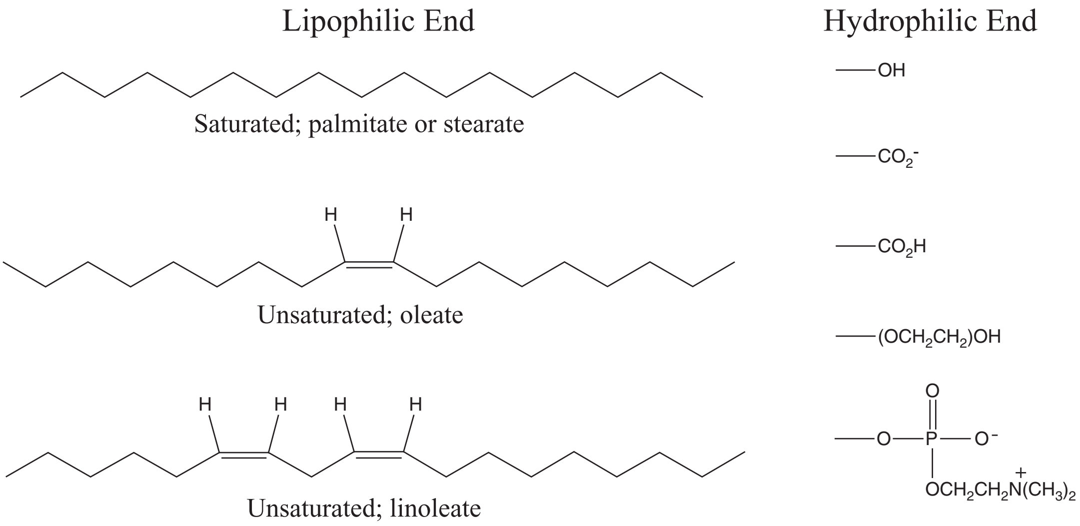


Figure 4.22 Typical hydrophilic and lipophilic components of food emulsifiers

Table 4.15 Functions and application of emulsifiers in confections

Function	Applications
Emulsification	Caramel, toffee, etc.
Lubrication/reduce stickiness	Caramel, licorice, tablets, etc.
Plasticizer	Gum
Viscosity control	Chocolates, coatings
Fat crystal modification	Chocolates, coatings
Bloom inhibitor	Coatings
Release agent	Molded candies
Control oil separation	Peanut butter candies

Table 4.16 Hydrophilic-lipophilic balance (HLB) values of various emulsifiers

Emulsifier	HLB
Sorbitan tristearate (STS)	2.1
Mono- and diglycerides	2.1–2.8
Lactylated monoglyceride	2.4
Glycerol monostearate	3.8
Lecithin	4.0
Sorbitan monostearate (SMS)	4.8
Polyglycerol esters (PGPR)	7–13
Polysorbate 60	14.9
Polysorbate 80	15.4

soluble, but also to an increasing extent on their physical orientation, or packing structure.

4.6.2.1 Characterization

Which phase, oil or water, an emulsifier prefers depends, at least in part, on the relative sizes of the hydrophilic and lipophilic groups. Emulsifiers with larger polar head groups (hydrophilic component) and smaller alkyl chains (lipophilic component) tend to be more in water and form water-in-oil emulsion. In contrast, those emulsifiers with smaller hydrophilic components and larger lipophilic components tend to be more soluble in fats and stabilize oil-in-water emulsions. The ratio of the hydrophilic head group to the lipophilic components of an emulsifier leads to characterization of the HLB (hydrophilic-lipophilic balance) number. The HLB values of common emulsifiers used in confections are shown in Table 4.16. Although HLB values are often a starting point to determine which emulsifier may work best in an application, it is only used as a guideline since other factors may also affect how well a specific emulsifier performs.

4.6.2.2 Emulsifier Types

Numerous emulsifiers are found in confections, with Figure 4.23 showing the chemical structure of some of the more important ones.

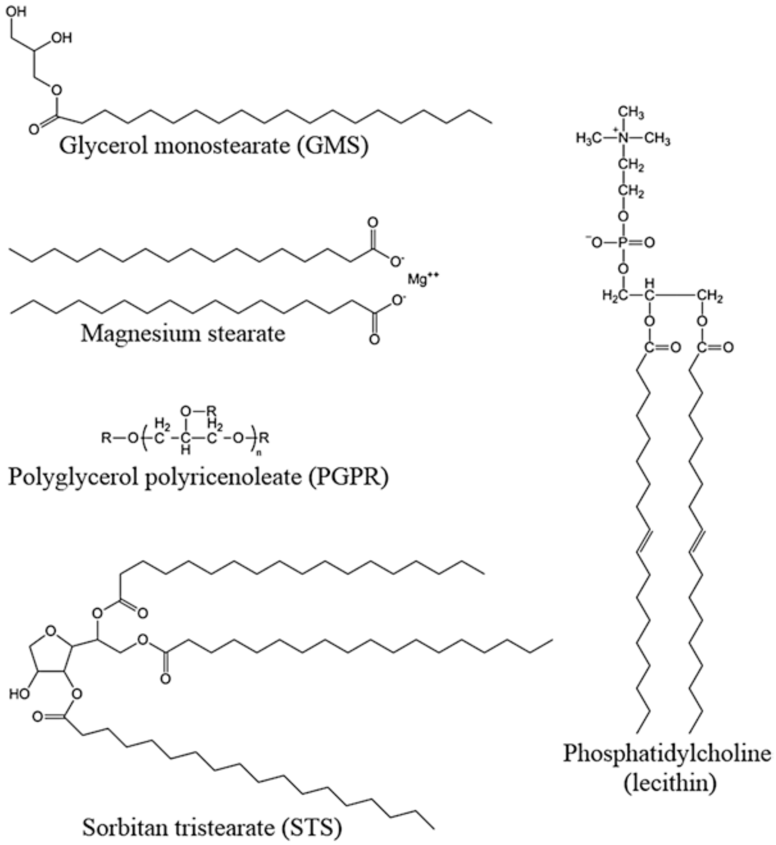


Figure 4.23 Chemical structures of various emulsifiers used in confections

Lecithin, a by-product of the soybean oil refining process, is easily the most common emulsifier found in confections. It is often used in caramel, fudge, and nougat (at 0.25–0.5%). A schematic depiction of the orientation of lecithin in caramel is shown in Figure 4.24, where it resides at the fat globule interface. In the caramel pre-mix, lecithin reduces the interfacial tension between oil and water, allowing smaller fat globules to be produced during mixing. It also helps prevent coalescence of the fat globules and oil separation during further processing and storage. Lecithin is also commonly used in chewing gum to help plasticize the gum base. Arguably, the widest use of lecithin in confections is in chocolates and coatings, where it provides a significant reduction in melt viscosity. The lecithin molecules orient at the sugar crystal surface, the most hydrophilic component of chocolate and where any water will reside, with the phosphatidyl group facing into the crystal and the fatty acids extending into the cocoa butter phase (Figure 4.25). By coating the hydrophilic surface of the sugar crystals, lecithin prevents these particles from aggregating and allows individual particles to easily move across one another in flow, thereby reducing viscosity. Typically, lecithin is used at levels less than 0.5%, depending on the phosphatide content. Higher levels have a negative effect on chocolate rheology (see Section 15.5.3).

Unrefined lecithin separated during soy oil processing contains about 65–70% phospatides and 30–35% soybean oil. The main phosphatides in unrefined soy lecithin include about 18% phosphatidyl choline, 15% phosphatidyl ethanolamine (also called cephalin) and 11% phosphatidyl inositol with 14–18% other types of

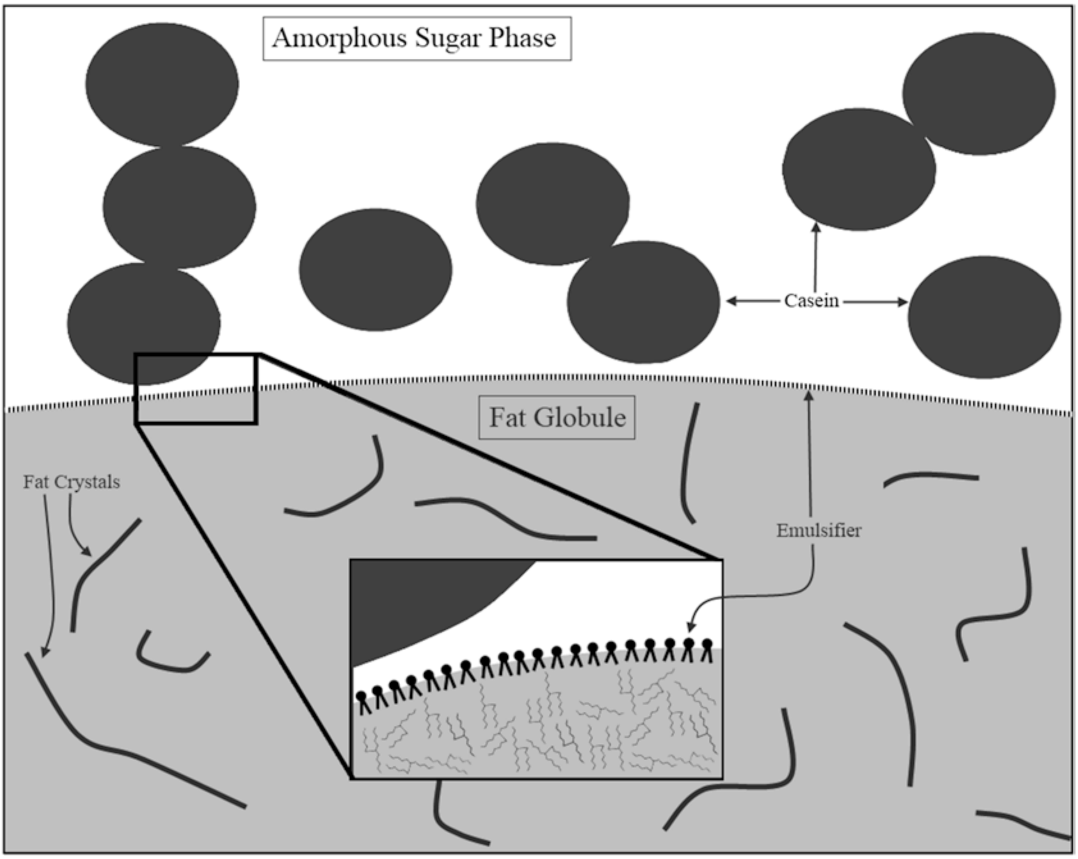


Figure 4.24 Orientation of emulsifier at the surface of a fat globule in caramel

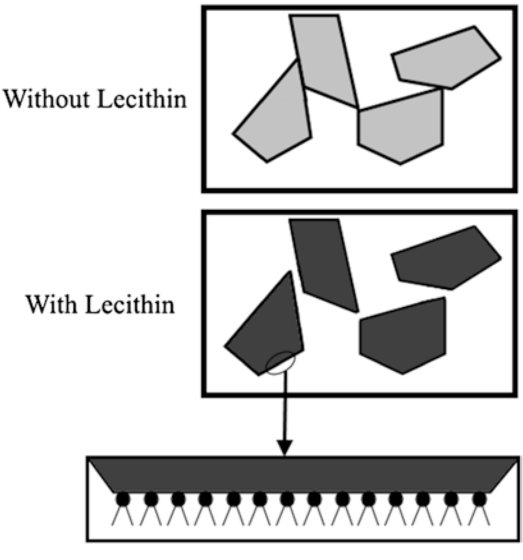


Figure 4.25 Orientation of lecithin at the surface of sugar crystals in chocolate. Without lecithin, the lipophobic sugar crystals aggregate, whereas with lecithin, the particles maintain separation

phospholipids. Unrefined lecithin also contains 13–16% glycolipids. Several variations in lecithin are also available including refined, fractionated and synthetic lecithin. Refined lecithin has the soy oil removed from unrefined lecithin by acetone extraction. The different phosphatides of commercial lecithin have also been fractionated with ethanol to increase the concentration of phosphatidyl choline (Wu and Wang 2003). Synthetic lecithins are produced by chemically reacting phosphate groups with glycerol and fatty acids to produce purified phosphatidyl choline. Lecithin from other materials, namely sunflower seed oil, is becoming more popular due to the negative image of soybean products (genetically modified).

Polyglycerol polyricinoleate, or PGPR, has recently become more widely used in confections, primarily in chocolate, because of its effects on rheological properties. PGPR (see

Figure 4.23) contains polymerized glycerol with polymerized ricinoleic acid, which is derived from castor oil. As with lecithin, PGPR is thought to orient at the sucrose crystal surface with the hydrophilic component (polymerized glycerol) facing in and the lipophilic part (polymerized ricinoleate) extending into the fat phase. Use of PGPR imparts a significant advantage for certain chocolate applications since it reduces yield stress with only minimal effect on plastic viscosity (see Section 15.5.3). This allows chocolate with PGPR to flow easily to fill molds with fine details. Use of PGPR also reduces the fat content needed in chocolate (for a set viscosity specification). PGPR (0.2%) in conjunction with lecithin (0.5%) in chocolate results in a fat reduction of about 8% cocoa butter.

Sorbitan tristearate (STS) is often used in compound coatings where it is thought to serve as a bloom inhibitor and enhance surface appearance. Although STS may aid crystallization, the mechanism proposed for bloom inhibition is that it slows the rate of polymorphic transition, thereby impeding one of the steps required for bloom formation. It is particularly advised for use in lauric-based (palm kernel oil) coatings for this purpose. Sorbitan monostearate (SMS) and polysorbate 60 are thought to have similar effects in compound coatings although are not as effective as STS. The exact mechanisms by which these emulsifiers serve to enhance stability in compound coatings are not known. Other emulsifiers, including mono- and diglycerides, diacetyl tartaric esters of monoglycerides (DATEM), acetylated monoglycerides, and proplylene glycol monoester, have been shown to have benefits in coatings (Weyland and Hartel 2008), although their use is not widespread.

Mono- and diglycerides (MAG/DAG) (see Figure 4.23) have surface-active properties that can be used to advantage in some confections. They can be used at levels of 1–2% in caramel to help provide emulsification and improve lubricity. Glycerol monostearate (GMS) is particularly useful in this application. MAG/DAG and GMS may also be used in chewy candies (fruit chews, nougat, etc.) to help reduce stickiness and enhance lubricity in both processing and consumption. They are particularly beneficial in reduced or low-fat formulations. Mono- and diglycerides may also be used in chewing gum to help plasticize the gum base and in starch-based confections like licorice to enhance pasting properties of the starch.

Certain types of emulsifiers are also employed as processing aids. For example, acetylated monoglycerides can be used as a release agent for various molded confections. The use of calcium or magnesium stearate in tableted confections provides another example of where emulsifiers are used to provide lubrication, in this case preventing the powder granulation from sticking to the die in the tablet press.

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Starches, Proteins, Pectin, and Gums

5

Hydrocolloids in foods are polysaccharides and proteins that serve to either thicken or gel aqueous solutions (Phillips and Williams 2009). In confections, starch, protein, pectin, and gums are the most important hydrocolloids. These hydrocolloids form gel structures that entrap an aqueous sugar matrix and provide structure to a soft solid confection.

5.1 Starch

In the confectionery industry, starch is an important ingredient that has been used for many years. Many starches have been modified to meet specific requirements. It is used as a molding medium to make impressions in which liquid fillings are deposited. Most importantly, though, starch is widely used as a gelling agent or as a stabilizing agent in a wide variety of starch-based jelly confections.

5.1.1 Description, Size and Shape

Starches are polysaccharides that contain numerous glucose units; they are also referred to as complex carbohydrates (Schink 1991). The number of individual glucose units, in part, is responsible for the many functional properties of starches. Starch, specifically cornstarch, and the degradation product of cornstarch, corn syrup, are important polysaccharides in the manufacturing of confections. Other major starch sources are wheat, rice, potato and tapioca.

Almost all starches consist of two glucose polymers, amylose and amylopectin. Amylose is a straight-chain polymer consisting of individual α-D-glucose molecules joined by 1,4-α glycosidic linkages. The number of individual units varies depending upon the source of the starch, and can exceed 1500 units, although the average molecular weight is about 10^6 Da. Amylopectin is a branched polymer consisting not only of α-D-glucose units joined by 1,4-α glycosidic linkages, but also contains glucose units joined by 1,6-α linkages (branch points). The branches can be 20–30 glucose units in length joined by 1,4-α linkages. Amylopectin is the larger of the two starch components, with average molecular weight of about 10^8 Da. The chemical structures of an amylose and an amylopectin starch molecule are illustrated in Figure 5.1. Most commercial starches contain between 20% and 30% amylose and the remainder amylopectin, calculated on a dry weight basis. Their moisture content varies between 12% and 15% depending on the ambient relative humidity. There are natural starches that fall outside these parameters – waxy cornstarch contains no amylose, and wrinkled pea starch contains no or very little amylopectin. In recent years, corn cultivars have been

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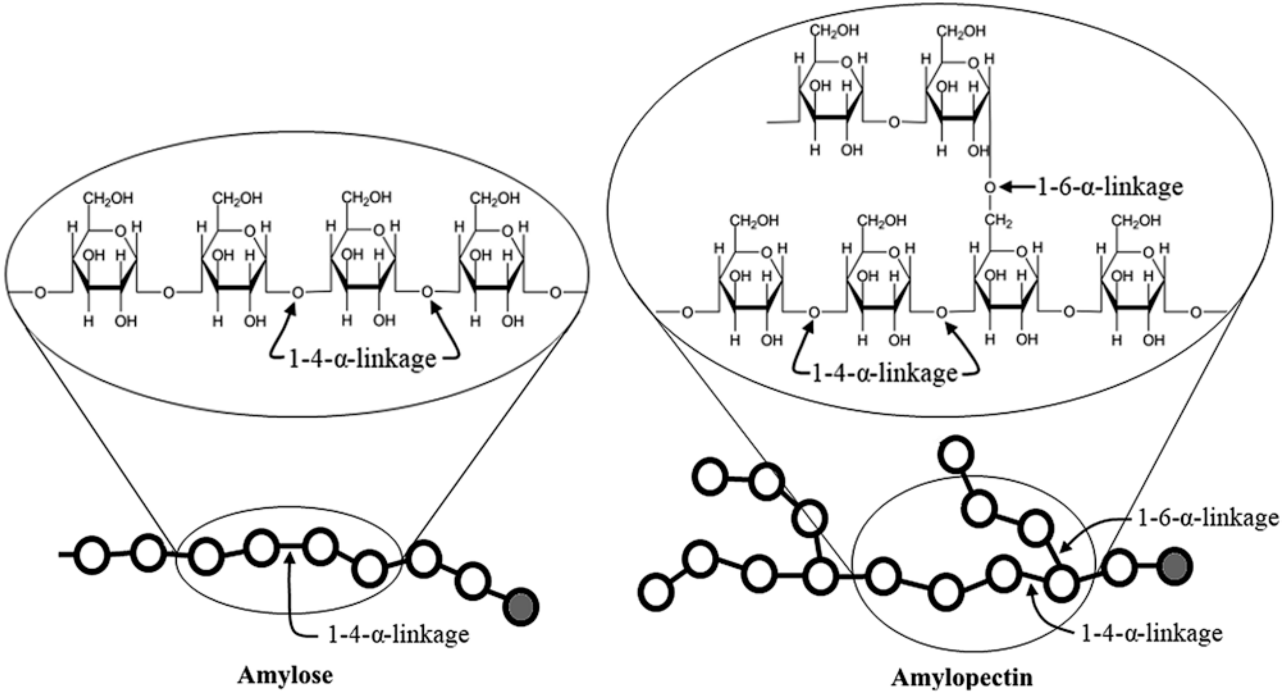

Figure 5.1 Chemical structure of amylose and amylopectin

Table 5.1 Proximate composition of dry corn (%)

Component	(%)
Moisture	16
Starch	61
Protein	9
Oil	3.8
Pentosans	5.3
Sugar	1.6
Minerals (ash)	1.3
Fiber	2.0

developed genetically with amylose contents between 50% and 70%. The proximate composition of dry corn is given in Table 5.1 (Corn Refiners Assoc 1989).

Starch particles are considered to be partially crystalline (Perez and Bertolt 2010). They show optical birefringence, exhibiting the classic "Maltese cross" under crossed polarizers in a polarizing light microscope. This property indicates some orderly orientation or crystallinity. The granules appear to be built up by deposition of alternating amorphous and semi-crystalline layers around a central nucleus, and when viewed under a microscope will clearly indicate the origin. Potato starch consists of large egg-shaped granules ranging in diameter between 15 and 100 μm; corn starch contains small granules of round and angular shapes 5–15 μm in size; and wheat starch also has varying sized granules, ranging from 2 to 53 μm.

5.1.2 Separation of Starches

A detailed discussion of the techniques used to separate starches from their raw product is beyond the scope of the chapter. A brief summary follows:

5.1.2.1 Corn Starch

A flow chart of the wet milling process to recover starch from corn is shown in Figure 5.2. Shelled corn is cleaned to remove possible metal contaminants and soil, after which it is steeped in warm water containing sulfur dioxide. The sulfur dioxide helps to break down the protein matter, acts as a bleaching agent and controls the microbial growth. Wet milling separates the germ, which is removed by gravity. To remove the hull, fiber and protein (gluten), additional grinding, screening and centrifugation. The starch is dried and either used as such or converted to other products – corn syrup, maltodextrin, glucose (dextrose) or high fructose corn syrup.

5.1.2.2 Wheat

Wheat flour has high protein content, containing 10% gluten. The starch is separated from the flour during a kneading process in running water. The starch is carried away as a slurry and allowed to settle out.

5.1.2.3 Potato, Arrowroot, Tapioca

Botanically these starch sources are tubers. They are first cleaned to remove all residual soil followed by grinding with water into a fluid mash. The mash is then strained to remove fiber and the suspended starch, which passes the sieve size, is repeatedly washed and eventually separated by centrifugation and dried.

5.1.3 Property of Starches

Starches vary in the percentage of amylose and amylopectin as well as the number of glucose units per chain. The straight chain fraction takes the form of a helix, which is capable of forming an inclusion product with iodine, giving starch suspensions the characteristic blue color. Each turn of the helix is made up of six glucose units and holds one molecule of iodine. Thus, the length of the amylose chain determines the color produced (Table 5.2).

In confections, starch is used in multiple different ways. Its primary use is as a gelling agent to create structure in jelly candies. However, starch granules can also be used for molding shapes (gummy and jelly candies, creams, marshmallow, etc.) or as an anti-stick agent (e.g., on marshmallows). When used as a gelling agent, its gelatinization temperature during cooking is important, whereas as a molding agent, its moisture properties are most important.

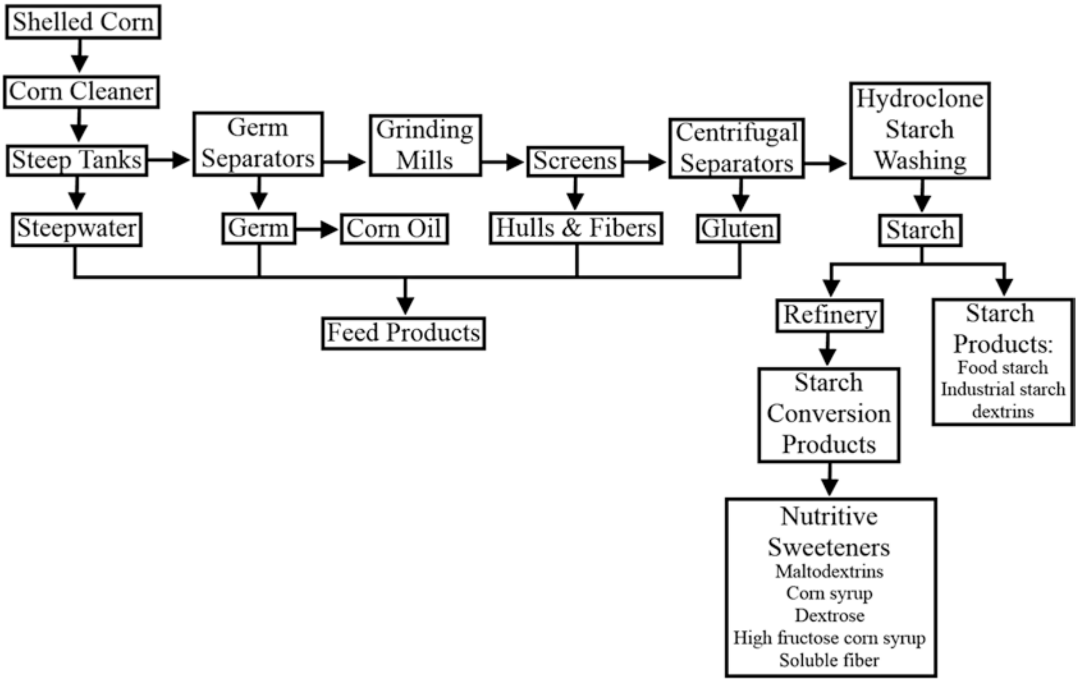

Figure 5.2 Flow chart of wet milling process to recover starch from corn

Table 5.2 Color of iodine inclusion by amylose of different chain length

Chain length	Number of helix turns	Color produced
12	2	None
12–15	2	Brown
20–30	3–5	Red
35–40	5–7	Purple
>45	9	Blue

5.1.3.1 Starch Gelatinization

Starch granules are completely insoluble in cold water. Only upon heating, or after being subjected to shear forces, and after some time, will water be taken up by starch. The point at which water up-take or swelling occurs is referred to as the gelatinization temperature, although gelatinization actually occurs over a temperature range as a slurry is heated. Gelatinization of starch granules is affected by a number of factors – pH, heating rate, shear forces, hydrogen bonding, presence of salt and sugar. Starches, because of the many hydroxyl groups, have great capacity to hydrogen bond. Water in dry starch is held between chains of starch molecules through hydrogen bonds. Starches could be dried to a point where there is no water separating the starch chains; however, the close association of the chains would make water up-take very difficult, if not impossible. To start gelatinization of starch, energy (heat) must be supplied to break the hydrogen bonds, and thus allow for water to enter and form new hydrogen bonds. The gelatinization process, therefore, is a continuous process of breaking hydrogen bonds and forming hydrogen bonds. It is far easier to start gelatinization in waxy cornstarch compared to wrinkled pea starch because waxy corn starch contains virtually no amylose, while wrinkled pea starch contains no amylopectin. An analogy might be to think of amylose as flat wooden boards (e.g., two-by-fours) and amylopectin as tree branches. In a rain storm, a pile of tree branches would most likely be wetted uniformly, while only the outside of a pile of two-by-fours would be wet, illustrating the difficulty to penetrate the straight chain molecules of starch. Data in Table 5.3 show the impact of the percent amylose content and granule size of starch on the gelatinization temperature. In the first set of starch sources (oat, triticale, corn bran), the amylose content is the same but the size of the granule increases, illustrating the effect of increased granule size on increased gelatinization temperature. In the second set of starch sources, both the amylose content and granule size increase, illustrating that with increasing amylose content and increasing granule size, gelatinization temperatures increase. In the third set of starch sources, the amylose content increases while the granule size is the same, illustrating that increasing amylose content also increases gelatinization temperature.

The effect of amylose content (%) in different starches on gelatinization time (min) is illustrated in Figure 5.3. Because of the difficulty of getting water into amylose, the starch with the highest amylose content has the longest onset time of gelatinization. Figure 5.4 illustrates the effect of temperature (Figure 5.4a), mixing speed (Figure 5.4b), pH value (Figure 5.4c) and other ingredients (Figure 5.4d) on the gelatinization time of corn starch. The change in temperature from 90 to 95 °C (Figure 5.4a), or the change in mixing speed from 100 to 200 rpm (Figure 5.4b) illustrates the effect of an increase in energy input. With greater energy input, higher temperature (95 °C) or higher rpm (200 rpm), the time of onset of gelatinization is reduced; however, once the maximum viscosity has been reached, at the higher energy inputs, breaking of hydrogen bonds results in loss of viscosity.

Table 5.3 The effect of amylose content and starch granule size on gelatinization temperature

Starch source	Amylose (%)	Size (μm)	Gelatinization temperature (°C)
Oat	24	10	53–59
Triticale	24	19	52–62
Corn bran	24	30	64–67
Corn	25	15	62–72
Sorghum	23–28	35	68–78
Barley	22	25	56–60
High amylose	52	25	67–80

5.1.3.2 Molding Starch

When using starch for starch molding of confections, it is important to know the moisture content in equilibrium at different temperature and relative humidity. The moisture content of the starch influences its ability to remove moisture from the deposited candy syrup and if not correct, can lead to defects on the candies produced (see Chapter 12).

The uptake of moisture is to a large extent a function of the amylose content of starch, but is also influenced by temperature. In Figure 5.5, the sorption isotherms (see Section 3.4) of corn starch and potato starch at different relative humidity are compared. At 75% relative humidity and 22 °C, corn starch (26% amylose content) has a moisture content of approximately 16%, while potato

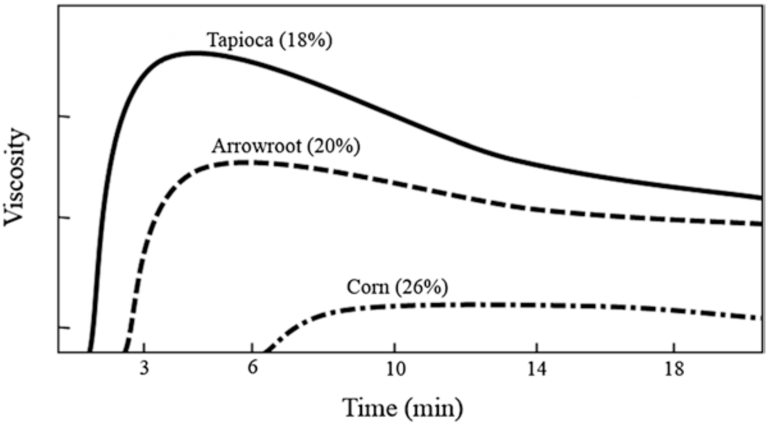

Figure 5.3 Effect of amylose content (%) in different starches on gelatinization time

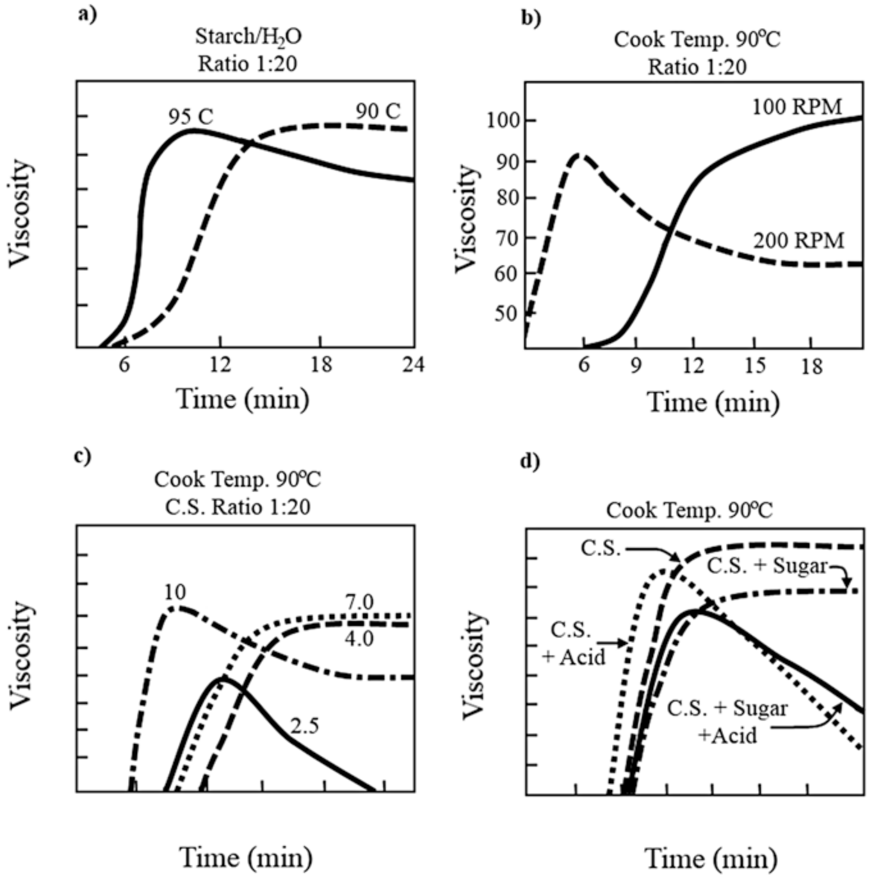

Figure 5.4 Gelatinization times of starch as affected by (**a**) temperature, (**b**) mixing speed, (**c**) pH, and (**d**) other ingredients. Starch to corn syrup (*CS*) ratio of 1:20 unless otherwise noted

starch (20% amylose content) has a moisture content of approximately 21%. The higher the amylose content the more difficult the moisture uptake (note the two-by-four analogy cited above). Further, the moisture content of corn starch decreases at increasing temperature (at constant relative humidity) as given in Table 5.4.

5.1.4 Modified Starches

The properties of starches can be modified by appropriate treatment to result in starches suitable for a specific purpose. Modification of starches can involve acid treatment, enzyme treatment, cross-linking, substitution, oxidation and heat.

5.1.4.1 Acid or Enzyme Treatment

Acid and enzyme treatment result in thin boiling starch, with reduced viscosity at elevated temperature. This is of value to the confectioner since the lower viscosity of the cooked slurry is more conducive to efficient depositing of the candy mass (see Chapter 12). When an aqueous slurry of corn starch is treated with hydrochloric or sulfuric acid at 0.5% and 50–60 °C for 12 h or longer, the granule structure is weakened or destroyed, as acid penetrates the intermicellar areas and hydrolyzes a small number of bonds. Acid modified starches yield low viscosity pastes that retain the ability to gel on cooling. Similarly, enzyme treatment will hydrolyze the starch molecule into smaller units resulting in lower viscosity.

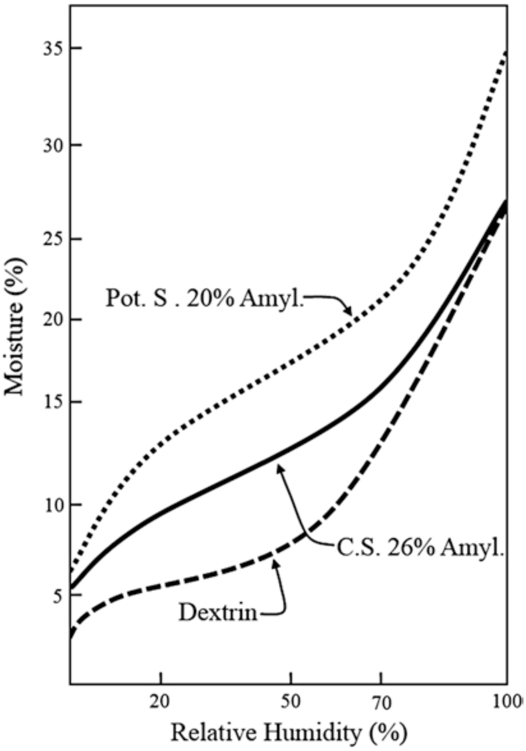

Figure 5.5 Sorption isotherms of dextrin, corn starch (*C.S.*), and potato starch (*Pot.S.*) at different relative humidities. *Amyl* amylose

Table 5.4 Moisture content (%) in corn starch at different temperatures and relative humidity values

Relative humidity (%)	Temperature (°C)				
	25	40	50	60	70
10	6.0	5.5	5.0	4.0	4.5
30	10.5	9.5	9.0	7.0	7.5
50	14.0	13.0	12.5	9.0	9.0
70	18.0	17.0	15.0	13.0	12.5
90	23.0	25.0	21.0	20.0	–

5.1.4.2 Cross-Linking

Cross-linking of starch involves the formation of chemical bonds between different areas in the granule, resulting in a starch more resistant to degradation upon swelling and a firmer gel. Small numbers of cross-links are required to bring about large changes in viscosity. One cross-link per 100,000 glucose units has a dramatic effect on the viscosity. Figure 5.6 compares the effect on viscosity of 1 cross-link per 1300 and 400 glucose units in corn starch. One cross-link per 1300 glucose units approximately doubles the viscosity on cooling.

Two methods are used to produce cross-linked starches. The first method involves treatment of an aqueous starch slurry with a mixture of adipic acid (1-4-butanedicarboxylic acid) and acetic anhydrides under mild alkaline conditions. After the treatment, the starch is washed and dried. The second method involves treatment of an aqueous starch slurry with phosphorus oxychloride or sodium trimetaphosphate under alkaline conditions. Cross-linking of starch makes the gels more resistant to damage by mechanical action. Natural starches, when swollen, are readily broken by mixing and subsequently lose viscosity. Cross-linking enables the viscosity to be maintained. In confections, cross-linked starches are used in fillings for shell chocolates where viscous and unchanging fluidity is required. Cross-linking does not prevent the amylose component in starch from subsequent gelling or syneresis. In cases where gelling is undesirable, cross-linking of starches void of amylose are used.

5.1.4.3 Substitution

The purpose of substitution reactions is to react some of the hydroxyl groups in starch with monofunctional reagents thereby introducing different substituents, and lowering the ability of the modified starch to form gels. Substituents include starch acetates, starch monophosphates, starch sodium octenyl succinate, and hydroxypropyl starch ether. The groups introduced with these reactions interfere in such a way that alignment of the molecule branches is prevented, thus giving greater stability during the freezing/thawing process. The substitution reactions can be performed on unmodified starches, or already modified starches such as acid or cross-linked starches.

5.1.4.4 Oxidized Starches

Oxidized starch is prepared by treating starch with hypochlorites. The reaction is carried out by combining a starch slurry with sodium hypochlorite. Carboxyl groups are formed under alkaline conditions on the linear portion of the starch molecule. This action minimizes association and

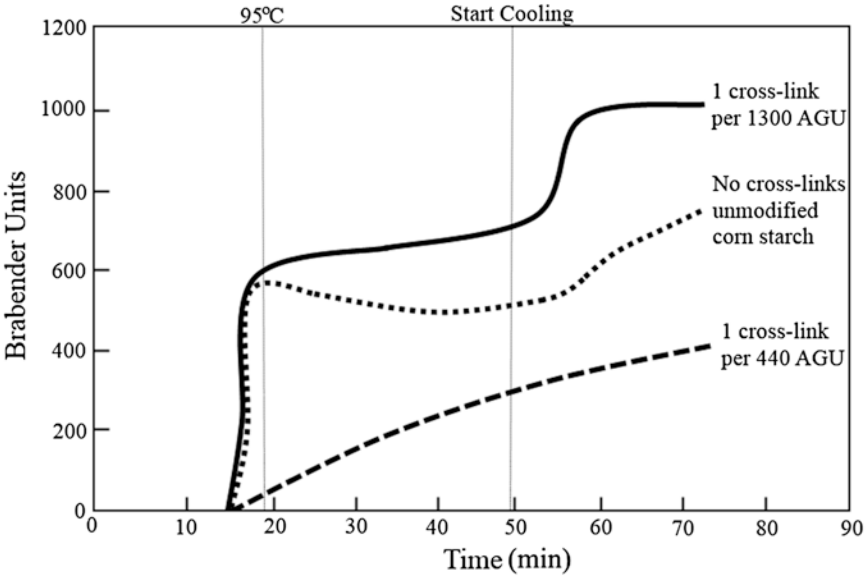

Figure 5.6 Effect of cross linking of starch on the gelatinization rate. Brabender units – arbitrary viscosity units generated by a Brabender consistometer

retrogradation. Other oxidative reactions may occur to form aldehyde or ketone groups. Oxidation of starch lessens the tendency toward gel formation by increasing the hydrophilic character of the starch.

5.1.4.5 Heat

Two modifications of starch can be the result of the application of heat. The first is the preparation of pregelatinized starch. It is prepared by heating a starch slurry on rollers that carry out the combined function of cooking and drying. These starches rapidly absorb moisture to form a paste. The second is the preparation of dextrin. Dextrinization is the action of heat on powdered starch under acidic conditions. The reaction products are hydrolysis and transglucosidation, with hydrolysis being the main reaction. Transglucosidation involves the hydrolysis of 1,4-α glucosidic bonds and recombination of the fragments with free hydroxyl groups forming new randomly branched structures. Dextrin is used, for example, in confectionery glazes.

5.1.4.6 Other Modifications

A small amount, 0.5%, of mineral oil is added to dried starch granule powder to produce molding starch. The oil improves the molding properties, or the ability to hold a depression formed in a flat surface of starch, and reduces dusting.

In recent years genetic engineering has enabled the production of high amylose corn and the manufacturing of high amylose corn starch. Because of the high amylose content, the starch gels rapidly and forms a very firm gel. However, it takes a great deal of energy to gel high-amylose starch so that pressure cooking is required.

5.2 Proteins

Proteins constitute a relatively small percentage in the total candy composition, but serve a number of important functions. They contribute to flavor and color through the Maillard reaction. They also influence the texture of candies. The use of egg albumin will give candies a soft and short texture, while gelatin will give candy a firm, elastic texture. In addition, proteins contribute to the nutritional content of candies. Milk in caramel and fudge, and nuts in several types of candies, are examples of proteins adding to the nutrient content of confections. This section will discuss the chemistry of proteins, their sources and their chemical and physical properties.

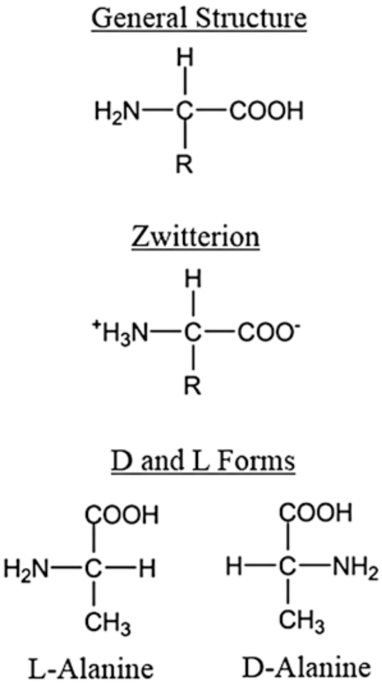

Figure 5.7 Structure of amino acids – general structure, zwitterion, D and L forms of alanine. *R* represents a carbon-based functional group, different for each amino acid

5.2.1 Protein Chemistry

Proteins are comprised of a sequence of amino acids, with each protein source having a unique amino acid fingerprint. The interactions between the amino acids, each of which has different chemical structure, lead to generation of the three-dimensional protein structure, or conformation. They also contribute to the specific protein functionality and reactions.

5.2.1.1 Amino Acids

α-Amino acids are the basic building blocks of proteins. Amino acids consist of a carbon atom to which covalently bonded is a hydrogen atom, an amine group, a carboxyl group and a R-group side chain (Figure 5.7). Amino acids differ only in the side chain (Figure 5.8), and the structural difference of the side-chain allows grouping amino acids as either hydrophobic, limited solubility in water, or hydrophilic, quite soluble in water. The hydrophobic or nonpolar amino acids are glycine (Gly), alanine (Ala), isoleucine (Ile), Leucine (Leu), methionine (Met), proline (Pro), valine (Val), phenylalanine (Phe), tryptophan (Trp), and tyrosine (Tyr). The hydrophilic or polar amino acids are the charged amino acids, argenine (Arg), aspartic acid (Asp), glutamic acid (Glu), histidine (His), and lysine (Lys), and the uncharged amino acids, serine (Ser), threonine (Thr), asparagine (Asn), glutamine (Gln), and Cystine (Cys). Therefore, the composition of the amino acids of a protein impacts its solubility. Proteins contain up to 20 primary amino acids. About half of the amino acids are essential amino acids for human nutrition, which means these amino acids cannot be synthesized in the body and must be supplied through proper nutrition. The percentage of essential amino acids in egg white, soybean meal, whey proteins and gelatin are compared in Table 5.5.

The α- carbon atom of an amino acid, with the exception of glycine, is an asymmetric carbon, meaning four different groups are attached to it. Thus, amino acids are optically active and for each asymmetric center two isomers exist represented by the D and L forms (Figure 5.7). All proteins found in nature contain only L-amino acids.

Since amino acids contain a carboxyl group (acidic) and amino group (basic), they behave as either acid or base, and thus amino acids can exist in three different ionized states, depending on the pH of the solution. At a pH value where both the carboxylic and amino groups are ionized, the amino acid molecule is a dipolar ion or zwitterion (Figure 5.8). The pH at which the dipolar ion is neutral is called the isoelectric point (pI) of the amino acid.

5.2.1.2 Protein Structure

In proteins, amino acids are linked by amide bonds or peptide bonds (Figure 5.9). A peptide bond is the linkage of the carboxyl group of one amino acid with the amino group of another amino acid and the elimination of a water molecule. The linkage of two, three or many amino acids is referred to as dipeptide, tripeptide or polypeptide, respectively. For example, aspartame, the intense sweetener, is a dipeptide. It is

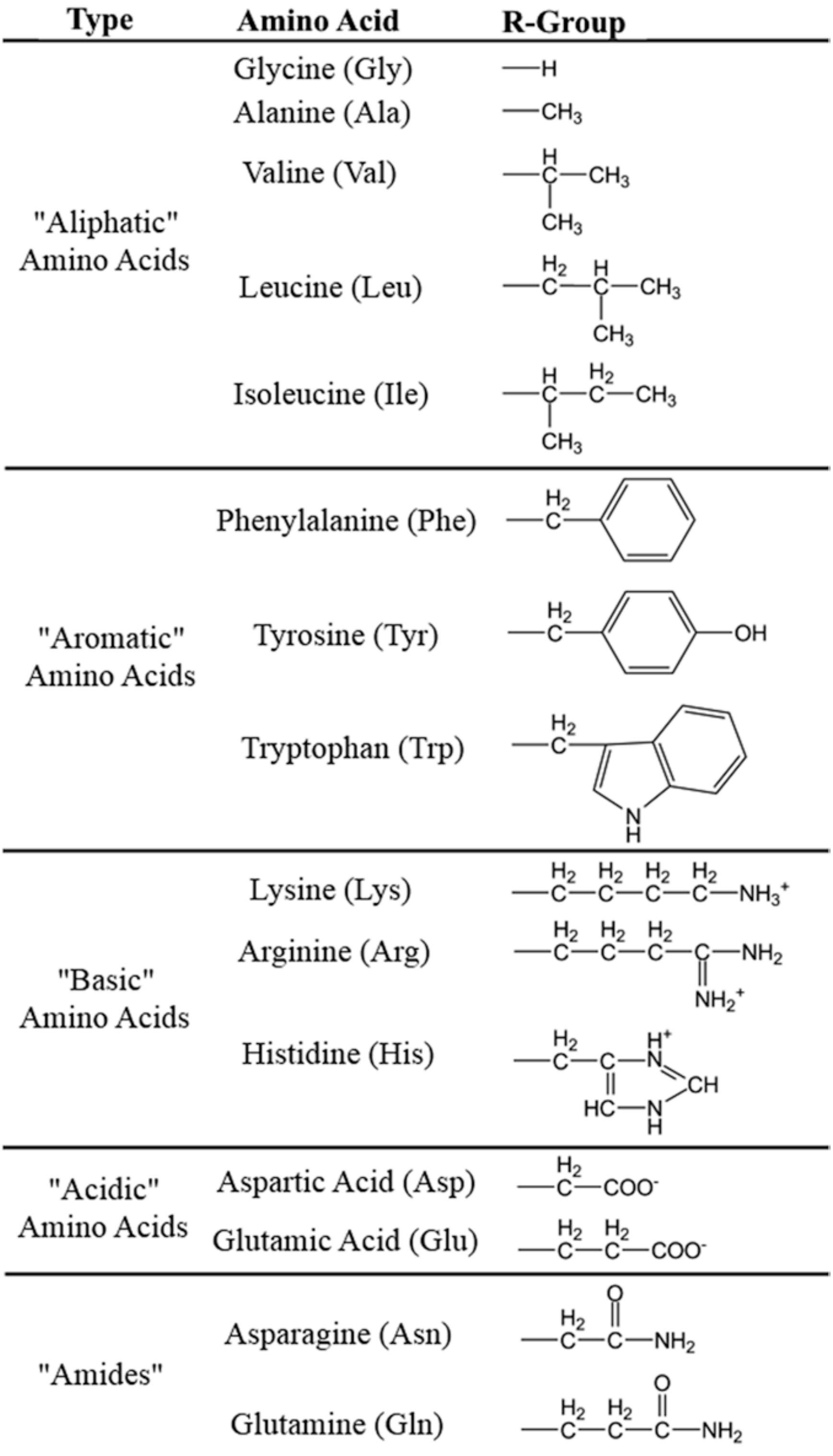

Figure 5.8 Side chains (R-groups) of amino acids

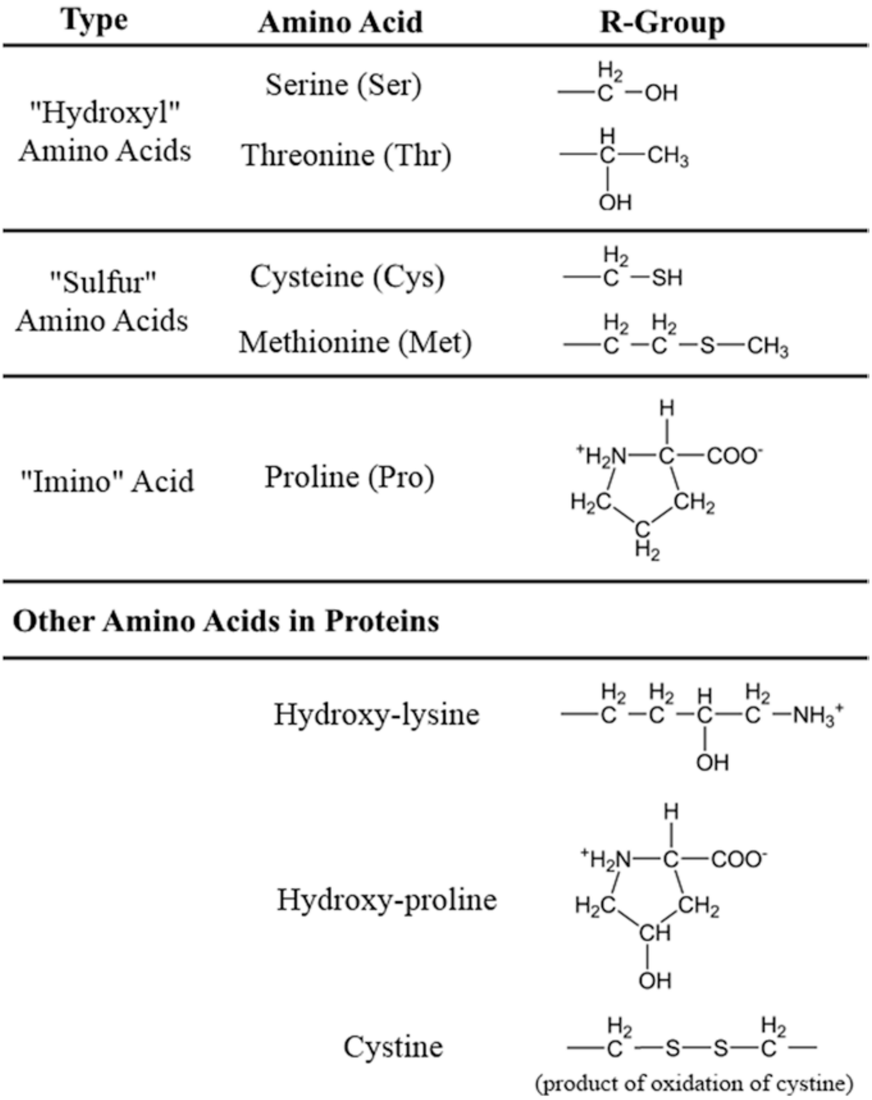

Figure 5.8 (continued)

Table 5.5 Comparison of essential amino acids in different proteins (%)

Amino acid	Whey protein	Egg protein	Gelatin	Soy protein
Isoleucine	6.6	6.4	1.4	4.2
Leucine	14.0	8.3	3.1	7.0
Lysine	10.9	7.1	4.1	5.1
Methionine	2.4	3.4	0.8	2.6
Cystine	3.2	2.3	0.1	–
Phenylalanine	4.1	5.8	2.1	7.3
Tyrosine	4.8	4.1	0.4	–
Threonine	6.7	5.2	2.2	3.5
Tryptophan	3.2	1.5	–	1.1
Valine	6.9	7.2	2.5	4.8

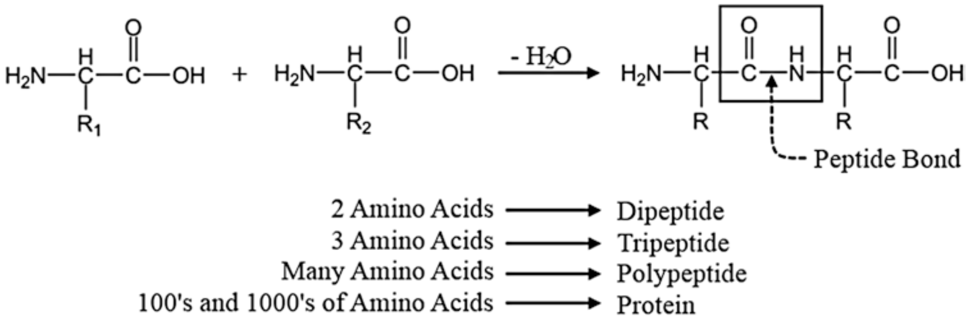

Figure 5.9 Peptide bond

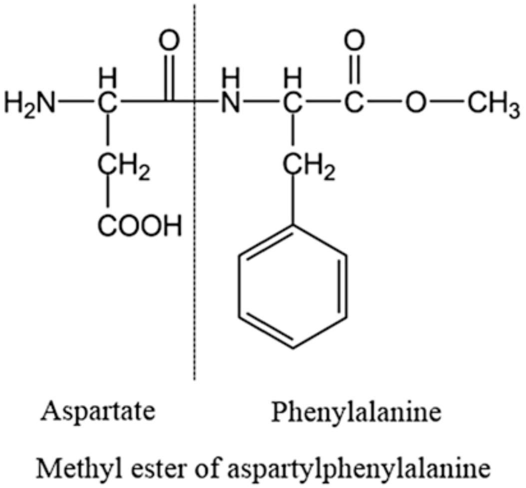

Figure 5.10 Structure of the dipeptide, aspartame

the methyl ester of the dipeptide containing the amino acids aspartic acid and phenylalanine (Figure 5.10).

Proteins contain 100 s and 1000 s of amino acids. Because of the molecular complexity, four levels of protein structure are recognized: primary, secondary, tertiary and quaternary. The primary structure is the linear sequence of the amino acids linked by amide or peptide linkages. The chain length and the sequence of amino acids determine the protein's biological properties and function.

The secondary structure refers to the local arrangement of amino acids at certain segments of the polypeptide chain. Two forms of secondary structures are found in proteins. These are the helical and sheet-like structures. They are stabilized through hydrogen bonding.

Tertiary structure refers to the arrangement of the entire polypeptide chain in space. The transformation of the linear configuration into the folded structure is a complex process. The most important aspect is that most of the hydrophobic amino acid residues reside at the interior of the protein (protected against contact with water) and most of the hydrophilic amino acid residues are at the protein-water interface.

Quaternary structure is the noncovalent association of more than one polypeptide chain in a protein. Depending on the number of polypeptide chains they are referred to as dimers, trimers, tetramers, and so on. These complexes are also referred to as oligomers and can either be homogeneous (two or more of the same polypeptide), or heterogeneous (two or more different polypeptides). Many food proteins exist as oligomers.

5.2.1.3 Protein Classification

Proteins are either classified as simple, conjugated or derived proteins.

5.2.1.3.1 Simple Proteins

Simple proteins yield amino acids on hydrolysis. Two important simple proteins in confections are the albumins and globulins. Albumins are soluble in neutral salt-free water. They are relatively low molecular weight proteins, and include egg albumin and lactalbumin and serum albumin in whey protein. Globulins are soluble in neutral salt solutions. They are almost insoluble in water. They include the serum globulins and β-lactoglobulin in milk and glycinin in soybeans.

5.2.1.3.2 Conjugated Proteins

Conjugated proteins contain a polypeptide part combined with a nonprotein component such as lipids, carbohydrates or nucleic acids. Two important conjugated proteins in confections are phosphoproteins and lipoproteins. Phosphoproteins include many important food proteins. Phosphate groups are linked to the hydroxyl groups of serine and threonine. They include casein of milk and phosphoproteins of egg yolk. Lipoproteins are a combination of lipids with protein. These proteins have excellent emulsification properties and occur in milk and egg yolk.

5.2.1.3.3 Derived Proteins

Derived proteins are partially hydrolyzed proteins derived by either chemical or enzymatic methods. They are soluble in water and not coagulated by heat. For example, soy protein hydrolysates find application as whipping agents.

5.2.1.4 Denaturation

Denaturation is a complex reaction that changes the molecular structure of a protein without breaking peptide bonds. The native structure of a protein is the result of various intermolecular forces (e.g., disulfide bonds) as well as interaction of protein groups with the surrounding water. Changes in structure are brought about by changes in the environment, namely change in pH, temperature, salt concentration, and so on. Subtle changes that do not alter the molecular structure substantially are referred to as conformational adaptability. Changes in the secondary, tertiary, and quaternary structure without cleavage of peptide bonds are referred to as denaturation. Denaturation always involves loss of biological activity and changes in the proteins functionality, and is generally thought of as undesirable. In food proteins, denaturation causes insolubility of a protein and losses in functional properties. In some instances, denaturation is desirable. Also, partially denatured proteins are more digestible and have better foaming and emulsification properties. Thermal denaturation is required for heat-induced gelation of proteins.

Proteins are denatured physically by heat, shear and pressure and chemically by pH, organic solvents or solutes, and salts. In candy processing, the denaturation is most likely caused by heat, shear and pH. For example, in the manufacturing of gelatin gummies, gelatin is added to the boiled sucrose/corn syrup mixture below 80 °C to avoid excessive denaturation of the gelatin at higher temperatures. An important property of proteins is their denaturation temperature, T_d. The T_d is defined as the temperature at the transition midpoint where the concentration ratio of the native protein and the denatured protein is 1. For example, the T_d of egg albumin is 76 °C while those of α-lactalbumin, β-lactoglobulin and soy glycinin are 83, 83 and 92 °C, respectively. Sucrose, glucose and corn syrups stabilize proteins against heat denaturation; the T_d of a protein is significantly increased in the presence of these additives.

High mechanical shear produced during whipping, for example, can also denature proteins. Since whipping incorporates air, the energy of the air-liquid interface is greater than that of the bulk phase and therefore proteins undergo denaturation at the interface.

At neutral pH (6–7), most proteins are stable. At both higher and lower pH values, the stability toward denaturation decreases as the net charge on the proteins change. It is for this reason that in the manufacturing of an acid gelatin candy that the acid is added last to avoid excessive denaturation.

5.2.2 Functional Properties

Although proteins are of great nutritional importance in foods, in confections they are used more for their functional properties. Functional properties of a protein are those properties that affect the characteristic of a product during processing, storage and consumption. For most proteins, these properties are experimentally determined; however, in some instances the structure of a protein can provide information as to the protein's functions. Protein functionality is the result of the protein interaction with water, with other protein, or changes in surface characteristics of the protein. Although proteins have a number of functional properties, the functional properties of most importance in confections are solubility, foaming, and binding with lipids and flavors.

5.2.2.1 Solubility

Although the solubility of a protein is not a true functional property, solubility impacts the functional properties of a protein. It is the interaction of the protein with water, and is influenced by the hydrophobic and ionic nature of the protein. Hydrophobic interaction of proteins results in decrease in solubility, while ionic interaction with water increases solubility. Both are influenced by pH, ionic strength and temperature. Above or below the protein's isoelectric pH, the protein is either positively or negatively charged. Proteins are least soluble at or around their isoelectric point – with no charge to provide stabilization, they easily aggregate and precipitate out of solution. The solubility increases with increasing positive or negative charges, as pH either goes up or down from the isoelectric point. For this reason, protein solubility follows a U-shape pattern with the lowest point at the isoelectric point.

Ionic strength is a function of salt concentration. At low concentrations (<0.5), ions neutralize charges on the surface of the protein, and depending on the characteristics of the protein surface will either decrease or increase the solubility. Under the same conditions, temperatures between 10 and 40 °C in general will increase solubility of a protein. Above 40 °C, denaturation will occur exposing more nonpolar groups and solubility will decrease.

Proteins can be classified into four groups based on their solubility characteristics. Albumins are those that are soluble in water at pH 6.6; globulins are those that are soluble in dilute salt solutions at pH 7.0; glutelins are those that are soluble only in acid (pH 2) or alkaline (pH 12) solutions; and prolamines are those soluble in 70% ethanol.

The solubility of most proteins increases with increasing temperature between 0 and 40 °C (32–104 °F). Above 40 °C, denaturation begins to occur. β – Casein, a milk protein, is one example of a protein that is more soluble at colder temperatures.

Table 5.6 Flavors generated by various amino acids

Amino acid	Typical flavor
Phenylalanine, glycine	Caramel-like
Leucine, arginine	Bread-like, toasted
Alanine	Nutty
Glutamine, lysine	Buttery
Arginine	Popcorn
Cysteine, glycine	Smoky, burnt
Methionine	Broth-like, beany

5.2.2.2 Flavor/Flavor Binding

Proteins are generally flavorless. They can however contribute to flavor either through chemical reactions forming flavor precursors or through flavor binding.

In the Maillard reaction (see Section 1.4.3.1), dicarbonyl compounds are formed that react with an amino acid resulting in aldehydes (Strecker degradation). The Stecker degradation product of glycine is formaldehyde, that of alanine is acetaldehyde, that of phenylalanine is phenylacetaldehyde, that of valine is 2-methyl propanal, and that of isoleucine is 2-methyl butanal. Not all generated flavors are necessarily desirable. Table 5.6 lists some typical flavors generated by various amino acids.

Proteins also bind both desirable and undesirable flavors. The undesirable flavors are those generated by lipid oxidation (i.e., aldehydes, ketones and alcohols). They are often bitter and are very difficult to remove and resist solvent extraction. Proteins also can bind desirable flavors and therefore act as flavor carriers. In order for a protein to function as a flavor carrier, the flavor must be tightly bound, remain bound during processing and should be released readily in the mouth.

5.2.2.3 Foaming

The formation and stability of a foam requires the presence of a surface active agent, or surfactant (see Section 4.6). This can either be a small molecule such as lecithin or a macromolecule such as a protein. Foams consist of an aqueous phase and a gaseous dispersed phase. The foaming ability of a protein relates to its ability to quickly adsorb at the air-water interface and to form a thin film so that large quantities of gas bubbles can be incorporated and stabilized. Foaming properties are evaluated by the ability to foam, foam capacity, and the stability. The foam capacity is expressed either as overrun or foaming power. The stability is expressed in terms of the time required to drain 50% of the liquid or 50% reduction in volume.

There are a number of factors that affect foam formation, including pH value, salt concentration, presence of sugars and/or lipids, and protein type and concentration. Foams are most stable at or near the protein's isoelectric point. At the isoelectric point, the lack of repulsive forces (no charge effects) promotes interaction of proteins and more protein is adsorbed at the interface. These two factors improve both the ability to foam and the stability.

Greater protein concentration increases foam stability. In general, protein concentrations are 1%, although with whey protein, higher concentrations are needed (2–5%). Partial denaturation (1 min at 70 °C) improves foam properties. This is because the mild heat treatment allows slight unfolding of the protein and thus allows for better adsorption at the interface. Heating for 5 min at 90 °C, even though the protein stays in solution, decreases the ability to foam. The reason for the decrease following such a heat treatment is the formation of high molecular weight polymers, which lack the ability to adsorb at the interface.

The effect of salt on foam formation depends on type and solubility of the protein in a salt solution. For some proteins, the ability to foam and the stability increase with increasing salt concentration. This is true for egg white and soy proteins, because the charges in these proteins are neutralized by the salts. However, the opposite is true for whey proteins. The difference in these proteins is the "salting in" of proteins, especially of β-lactoglobulin. In general, proteins that are neutralized by salt, or "salted out", exhibit improved ability to foam. Proteins that are "salted in" exhibit poor ability to foam. The presence of calcium and/or magnesium improves both the ability to foam and the stability.

Sugars impair foam capacity or the ability to foam, but increase the stability. The positive effect on stability is the increase in viscosity that reduces the drainage of lamella fluid. The negative effect on the ability to foam is that the increased stability does not allow the protein to unfold at the interface. Thus, when producing a foam, it is most desirable that the sugar be added at the end of the whipping process, although this is rarely done in commercial confectionery processing.

Lipids in concentrations greater than 0.5% impair foaming. This is because lipids are more surface active and impair adsorption of proteins. Since lipid films lack cohesiveness, the internal pressure causes the bubbles to expand and collapse. If lipids are required in the presence of a foam, they should be added last in the process and carefully folded in to avoid loss of aeration.

5.2.3 Proteins Used in Confections

Proteins of interest in the manufacturing of confections are gelatin, egg white, milk, and soy proteins.

5.2.3.1 Gelatin

Gelatin is a protein derived by extraction and partial hydrolysis of collagen, a protein found in bones, hides, connective tissue, and skins of animals. Although cattle and pigs are the main sources, gelatin from fish may see increased use in the future based on religious concerns. There are two extraction processes: acid extraction produces Type A gelatin whereas Type B gelatin is produced through an alkali extraction.

Pork skins are the most significant raw material source in the United States for the production of edible Type A gelatin. Skins are soaked in cold dilute mineral acid for several hours. After maximum swelling has occurred, the acid is washed out and the skins are extracted with hot water. Typical extractions are carried out at a pH range between 3.0 and 6.0. The starting temperature for the extraction process is between 50 and 60 °C (122 and 140 °F) with subsequent extraction being made with increased temperatures. The final extraction is made at a temperature close to the boiling point. The initial extraction provides a superior gelatin. Early extractions contain higher molecular weight molecules, have higher viscosity, higher gel strength and the least color. The extracts are filtered and concentrated by either vacuum concentration or ultrafiltration. The concentrates are chilled and deposited on a belt for drying. The temperature of the drying process starts at 30 °C (86 °F) and ends at 70 °C (158 °F). The dried material, which has moisture content of 1%, is then cut and ground.

For Type B gelatin, bones are first subjected to an acid treatment to remove all the minerals. This process produces a spongy material known as ossein. The ossein and hides are then subjected to a lengthy lime treatment. During this treatment, some deamination of the collagen occurs. After the lime has been removed with cold water, the gelatin is extracted by successive washings with hot water. The liming of bones and hides produces Type B gelatin, with an isoelectric point between pH 4.8 and 5.2.

The amino acid composition of gelatin is given in Table 5.7 and some parameters of edible gelatin are given in Table 5.8. Although the differences between the two types of gelatin are small, they are not necessarily interchangeable. For the most part, they are easily substituted for one another.

Gelatin is rated by what is known as Bloom rating. The Bloom rating is the firmness of a 6.67% gelatin solution equilibrated at 10 °C for 17 h. The firmness is measured with a Bloom gelometer. The instrument measures the weight of lead shot required to depress a standard plunger (12.7 mm dia.) a distance of four mm into the gel surface. The weight of the lead shot is equal to the Bloom rating. In general, gelatins with higher average molecular weight form firmer gels (higher Bloom rating).

The properties of gelatin solutions are influenced by temperature, pH, ash content, and concentration. With time and increasing temperature, the degradation of gelatin is significantly enhanced (Figure 5.11). Holding gelatin solutions at elevated temperatures is undesirable because this degradation of the structure results in loss of Bloom strength and less firm gel. Gelatin solutions are most stable at pH range between 5.0 and 6.0. Either lowering or raising the pH will accelerate degradation (Figure 5.12) and result in loss of Bloom strength. As might be expected, with increasing concentration (increasing molecular weight), the viscosity of the gelatin solution increases (Figure 5.13). Bloom strength also increases accordingly. The ash or mineral content will act as a catalyst and accelerate the degradation. Typical ash composition of both types of gelatin is given in Table 5.9. These values show significant differences between the two types, which further suggests that the two types are not necessarily interchangeable.

Table 5.7 Gelatin amino acid composition

Amino acid	Content (%)
Proline	30
Glycine	30
Glutamic acid	12
Alanine	9
Arginine	8
Aspartic acid	6
Others	8

Table 5.8 Parameters of edible gelatin

	Type A	Type B
pH	3.8–5.5	5.0–7.5
Isoelectric point	7.0–9.0	4.7–5.4
Bloom strength	50–300	50–275
Ash content (%)	0.3–2.0	0.5–2.0

5.2.3.2 Milk Proteins

Milk proteins serve as functional ingredients as well as add significantly to the nutritional value of candies. Milk protein can be divided into two groups, the caseins and the serum proteins (whey proteins). The caseins comprise 78% and the whey proteins comprise 17% of the total weight. The composition of proteins in milk is given in Table 5.10. The two protein components can easily be separated.

Milk protein concentrates are made by ultrafiltration of milk to concentrate the proteins from the smaller molecular weight components in milk

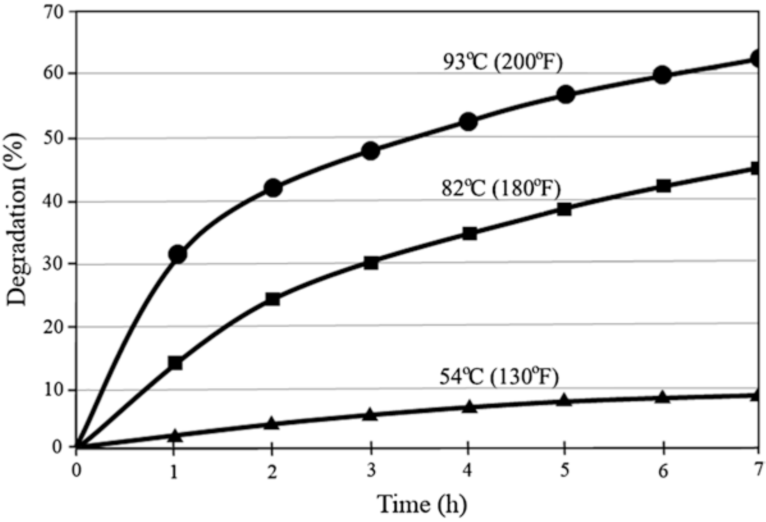

Figure 5.11 Bloom strength degradation (%) at different temperature at pH 6.0

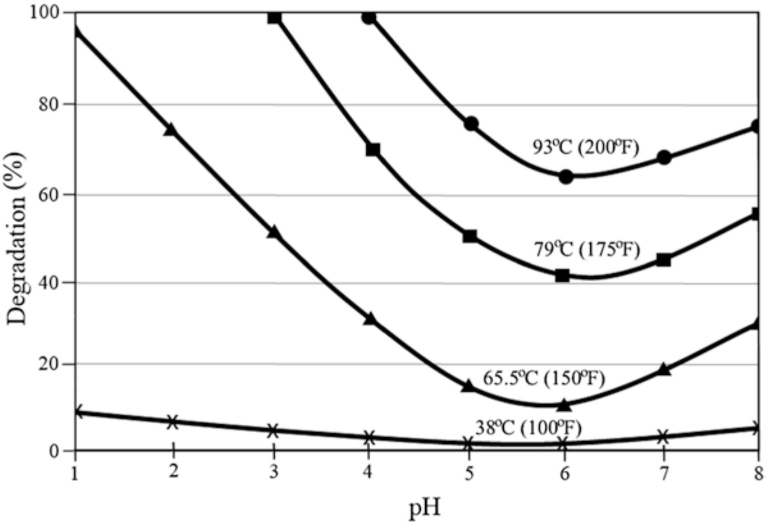

Figure 5.12 Bloom strength degradation after 7 h at different pH and temperature

(lactose, salts, etc.). The concentrates must have a minimum protein content of 40%, but can be as high as 90% (milk protein isolate). Higher protein content means, conversely, lower lactose content. Since they are created from milk solids, the protein breakdown remains the same as for intact milk, with a mixture of caseins and whey proteins. The reduced lactose content and increase protein content provide interesting opportunities in confections, particularly those with enhanced protein levels.

5.2.3.3 Whey Proteins

In recent years great advances have taken place in utilizing whey as an ingredient. Today, a number of whey-based products are available, including condensed/dried whey, demineralized whey, delactosed whey, whey protein concentrate, whey isolates, and individual whey proteins. The major whey proteins are listed in Table 5.10. Typical compositions of some concentrated whey products are listed in Table 5.11.

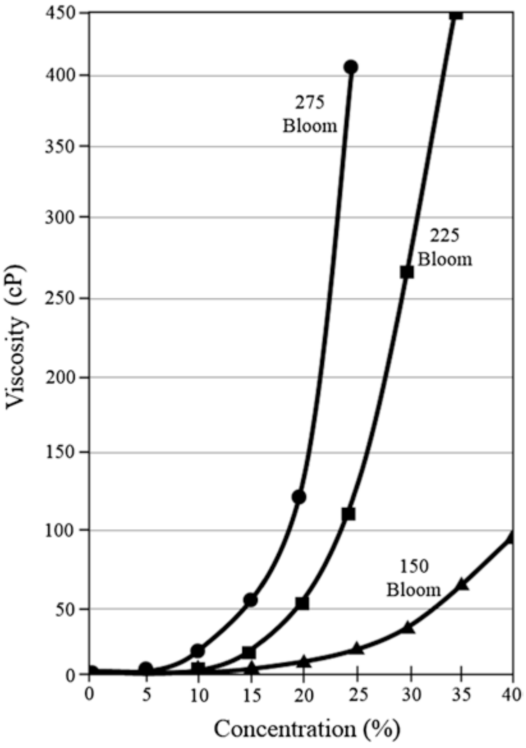

Figure 5.13 Effect of gelatin concentration on the viscosity of gelatin solutions made with different gelatin grades

Table 5.9 Typical ash composition (in ppm) of gelatin

	Type A	Type B
Sodium	500 ± 200	3600 ± 1400
Iron	4 ± 2	15 ± 10
Lead	0.002 ± 0.001	0.005 ± 0.002
Zinc	1.5 ± 0.5	5 ± 3
Calcium	90 ± 30	900 ± 100
Potassium	125 ± 50	330 ± 50

Table 5.10 Composition of proteins in milk

Protein	Concentration (g/L milk)
Caseins	
α_{s1}-casein	10.0
α_{s2}-casein	2.6
β-casein	9.8
κ-casein	3.3
Whey proteins	
β-lactoglobulin	3.2
α-lactalbumin	1.2
Serum albumin	0.4
Immunoglobulin-G	0.8

Table 5.11 Typical composition (%) of whey and whey protein concentrates (Smith 2008)

	Whey concentrate	Whey protein concentrate	Whey protein isolate
Moisture	5	4	1
Fat	1	4–6	1
Protein	13	33–77	93
Lactose	73	9–53	3
Ash	8	4–7	5

Table 5.12 Whipping and foaming properties of whey and egg proteins

	Whey protein	Egg albumin
pH	9.0	9.0
Color of foam	White	White
Volume (cm^3)	180	175
Drainage after 5 min	12	10
Specific foam volume (mL/g)	10	12

Whey proteins have both hydrophilic and hydrophobic areas and thus, they can act as emulsifiers. They are a very good whipping and foaming agent. In Table 5.12, the foaming and whipping abilities of whey proteins are compared to egg proteins. These data show that whey protein can be substituted for egg protein in many applications where foaming is important. Whey proteins that have not been denatured by heat have excellent solubility over a wide pH range. Heating to temperatures of above 70 °C can cause partial loss of solubility between pH 3 and 5. Under certain heating conditions, whey proteins will form irreversible gels entrapping water and thus preventing moisture losses. Whey proteins are also excellent sources of the essential amino acids. The data in Table 5.13 compares the essential amino acids found in whey proteins and egg albumin.

Whey proteins find applications in confections in, for example, caramel, dulce de leche and marshmallow/frappé. Because of their different properties compared to caseins, moderate changes in texture result from replacing milk proteins (caseins plus whey proteins) with whey proteins.

Table 5.13 Essential amino acids (%) in whey protein and egg albumin

Amino acid	Whey protein	Egg albumin
Isoleucine	6.55	6.45
Leucine	14.0	8.3
Lysine	10.0	7.05
Methionine	2.35	3.4
Cysteine	3.15	2.25
Phenylalinine	4.05	5.8
Tyrosine	4.8	4.05
Threonine	6.7	5.15
Tryptophan	3.2	1.5
Valine	6.85	7.15
Total	**62.55**	**51.1**

5.2.3.4 Egg Albumin

Egg albumins are simple proteins in that they yield only amino acids on hydrolysis. They are water soluble and have relatively low molecular weight. Egg white contains at least eight different proteins, the most abundant of which are ovalbumin, conalbumin, and andovomucoid. These three proteins account for 78% of the protein content in egg white. Ovalbumin is a phosphoprotein with a molecular weight of 45,000. It is a conjugated protein because upon hydrolysis it yields not only amino acid but also a small amount of carbohydrate. The carbohydrate is present as a polysaccharide. Ovalbumin is readily denatured by heat. Conalbumin is a much larger molecule with a molecular weight of 70,000. It is capable of iron binding, a property that is lost after heat degradation. Andovomucoid is a glycoprotein. It has a molecular weight of 27,000–29,000 containing mannose and glucosamine and is highly resistant to denaturation. Egg white is available in liquid or dried form. Liquid eggs are marketed in the frozen state. The liquid form contains 11% protein while the dry form contains 83%.

Egg white is used in candies as a whipping and foaming agent. The whipping and foaming properties are listed in Table 5.12, in comparison to those of whey protein. The data suggest that substituting whey proteins for egg white proteins is possible.

Table 5.14 Comparative foaming power of different protein solutions at pH 8.0

Protein	Foaming power at 0.5% (w/v) protein concentration (%)
Soy protein (acid hydrolyzed)	500
Gelatin (acid processed pig skins)	750
Egg albumin	250
Whey protein isolate	600

5.2.3.5 Soy Protein

Soy protein is a good source of essential amino acids except for methionine and tryptophan. It is particularly valuable because of its high lysine content, which is generally low in plant proteins. At pH values above and below the isoelectric point, soy proteins are soluble in water or dilute salt solutions. They are therefore classified as globulins. Soy protein is a complex mixture of several proteins. Starch gel electrophoresis, depending upon buffers used, reveal 14 or 15 protein bands. Heating of soybeans makes the protein more insoluble. Soy whey proteins are obtained after acid precipitation of the proteins from solution. The solution contains the albumins, globulins, water soluble carbohydrates, nonprotein nitrogen, salts and vitamins. Soy protein is available as proteins and protein isolates.

Off-flavors in soy hydrolysate products have been a limiting factor in their application; however, newer technologies have significantly reduced the off-flavors. Soy protein is used in candy as whipping and foaming agents. Data in Table 5.14 compares the ability to foam (foaming power) of soy proteins to that of gelatin, egg albumin and whey protein isolates. Nougat is one example where soy proteins have been used as aerating agents.

5.2.3.6 Other Proteins

New proteins are continually being promoted as new ingredients for confections, particularly those with functional properties. These might include proteins from peas, pumpkin seeds, lupine, rice and algae. Further, certain specific amino acids (e.g., lysine) may be added for functional benefits.

5.3 Pectin

Pectic substances are located in the middle lamella of plant cell walls. Their function is the movement of water and as cementing material for cellulose. When pectic substances are acid hydrolyzed, pectin is formed. When pectin is extracted, standardized, and in some cases modified by chemical or enzymatic treatment, it becomes one of the most valuable gelling agents for the manufacturing of candies.

Pectin is present in all fruits in variable amounts. It is also found in some roots like beets and carrots and in tubers like potatoes. Commercially, pectin is produced from apple pomace or citrus peels. Pectins in lemon and lime are most easily extracted and yield the highest quality. Apple pomace contains between 15% and 20% pectin, whereas citrus peels contain between 30% and 35% pectin. Pectins are extracted with a warm acidic solution and precipitated with alcohol. The precipitate is washed, squeezed, vacuum dried and ground to obtain a powder with a water content of 6–10%.

In confections, pectin is used as a gelling agent in such products as fruit slices, fruit jellies, Turkish delight, and chocolate-enrobed centers. Pectin forms a very clear gel, which is a very attractive property.

5.3.1 Pectin Chemistry

Pectins are galacturonoglycans [poly(α-D-galactopyranosyluronic acid)] with various content of methyl esters. The key feature of all pectin molecules is a linear chain of (1–4) linked α-D-galactopyranosyluronic acid units (Figure 5.14). The word pectin refers to a family of compounds known as pectic substances. In all pectins, some of the carboxyl groups are in the methyl ester form. Polygalacturonic polymers with some of the carboxyl groups esterified are referred to as pectinic acid, without esterification they are referred to as pectic acid. The remaining free carboxyl groups may be partially or fully neutralized as sodium, potassium or ammonium carboxylate groups. They are mostly in the sodium salt form. In addition, sugars like L-rhamnose are present. The α-L-rhamnopyranosyl units seem to be inserted into the polymer at rather regular intervals. Some pectins contain covalently attached, highly branched arabinogalactan chains and/or side chains composed of D-xylosyl units. The insertion of sugars as well as the presence of side chains may limit chain association. During gelling, association of unbranched pectins are formed when the negative charges of the carboxylate groups are neutralized by the addition of acid, when hydration is reduced by the addition of sugar, and/or when pectinic acid polymer chains are bridged by calcium ions.

5.3.1.1 Methoxylation

When more than half of the carboxyl groups are in the methyl ester form ($COOCH_3$), the pectins are classified as high-methoxyl (HM) pectins, the remaining carboxyl groups will be present as a mixture of free acid and salt forms. Pectins with less than half of the carboxyl groups in the methyl

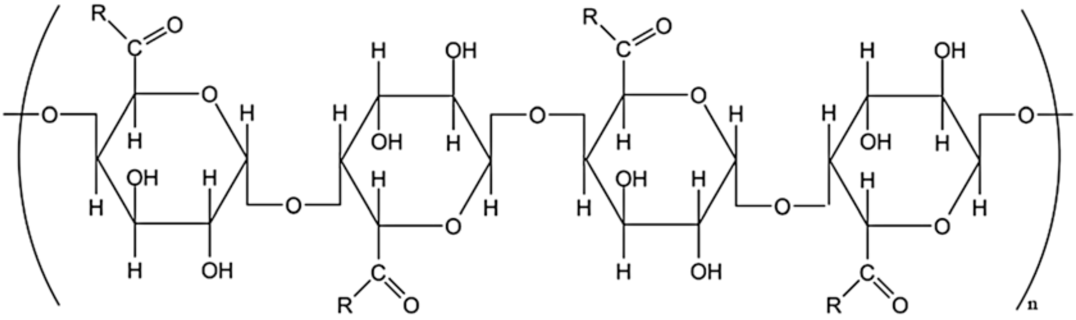

Figure 5.14 Structure of pectin. Pectic acids: R = OH; Methoxylated pectins (pectinic acids): R = OCH_3; Amidated pectins: R = ONH_2

Table 5.15 High methoxyl pectins

Type	Esterification (%)	Soluble solids (%)	Setting temperature (°C)	pH range
Rapid set	70–76	60–70	75–85	3.1–3.6
Medium set	68–70	60–70	55–75	3.0–3.3
Slow set	60–68	60–70	46–60	2.8–3.2
Confectioners buffered	60–66	75–80	90–95	–

ester form are referred to as low-methoxyl (LM) pectins. Treatment of these pectins with ammonia in methanol converts some methyl ester groups to carboxamide groups (15–25%). The latter pectins are referred to as amidated (LM).

5.3.1.1.1 High Methoxyl Pectin

Several grades of HM pectins are manufactured and the choice for making pectin jelly candies depends on the final usage (Table 5.15). Gel strength is influenced by a number of factors. Rate of heating – rapid heating to the desired solid content should take less than 15 min. Prolonged heating will cause excessive conversion of sucrose, degradation of pectin and loss of gel strength. Depositing of the jelly candy should be rapid to prevent similar changes. Premature setting will occur if the temperature prior to depositing drops below the setting temperature. Gel strength can also be lost because of incomplete solubilization of the pectin. It is general practice to mix the pectin powder thoroughly with eight to ten parts of sugar. This mixture is than added to water with rapid mixing, and thus the lumping of pectin is prevented.

5.3.1.1.2 Low Methoxyl Pectin

Table 5.16 gives the types of LM pectins available**.** As stated earlier, in contrast to HM pectin, sugar and acid are not essential for gel formation of LM pectin. Gels with solids content as low as 2% and pH close to neutrality can be prepared. The factors affecting gel strength discussed under HM pectin also apply to LM pectin. Although calcium salts are added by the manufacturer, it is sometimes necessary to make adjustments or further additions, because of the variability in water supply (see Chapter 3). Buffer salts are added to prevent pre-gelation. The advantage of the addition of buffer salts is that finished cooked candy mass can be held for a limited time before depositing without significant loss of gel strength. Salts used for this purpose are sodium citrate and tetrasodium pyrophosphate. They are added in quantities between 0.2% and 0.5% of the final jelly.

Table 5.16 Low methoxyl pectins

Type	Esterification (%)	Soluble solids (%)	Setting temperature (°C)	pH range
A	45–53	50–70	–	2.8–3.3
B	40–50	40–65	–	2.8–3.5
C	40–50	60–70	60–70	3.5–4.0
		75–80	85–95	4.0–5.2
D	32–37	20–50	–	2.8–3.2

5.3.1.2 Gelling Mechanisms

HM pectin solutions gel when sufficient sugar and acid are present. As the pH is lowered, the charged and hydrated carboxyl groups are neutralized and become less hydrated. This allows for association of portions of the polymer chains, forming junctions and a network of polymer chains that are able to entrap aqueous solutions (sugar). The sugar competes for water hydration, reduces solvation of the chain and thus allows interaction. The optimum pH for rapid setting of HM pectin is between pH 2.9 and 3.6. Below pH 2.9, hydrolysis of the pectin chain occurs, resulting in syneresis.

The degree of esterification above 50% determines the behavior of gel formation, specifically the rate of set. Higher degree of esterification means a higher temperature of set. If sugar is present, as in candy, because of the competition for water by sugar, the set temperature rises. Thus, the rate of setting can be controlled and premature setting is prevented. Pectins dissolve in water and partially dissociate to form -COO$^-$ ions resulting in a negative charge on the molecule and thus producing a repulsive force. Sugar, because of the competition for water, reduces the solubility of pectin, and the addition of acid neutralizes the charges allowing for interaction of the molecules and the formation of junction zones. Another factor that can be important is the presence of buffer salts such as sodium citrate or sodium polyphosphates. They not only influence the set temperature but also the rate of set.

LM pectins only gel in the presence of calcium cations, which will form cross-linkages between the chains. Increasing the concentration of calcium cations increases the gel temperature and gel strength. LM pectins do not require sugar for gelation; thus, the manufacturing of low-sugar (or sugar alcohol) gels is possible. The advantage of using LM pectin in candies is the jellies can be made with pectin, sugar, and calcium salt with or without the addition of acid. The use of calcium chloride will give a rapid set, whereas tricalcium citrate or calcium sulfate, because of lower solubility in water, will give slower set. Normal addition of these salts is between 0.05% and 0.1% of the final jelly.

Amidated pectins are produced by ammonia treatment of HM pectins. In this process, the methoxyl groups are partially replaced by $-COONH_2$ groups. Approximately 15–25% of the acid groups are substituted. Amidated LM pectins have certain advantages over normal LM pectins. They tolerate a wider range of calcium salts and will set more rapidly, and they tolerate a wider range of soluble solids. The gels are thermoreversible; that is, they melt on heating and set again when cooled. They also have shear thinning properties; just below the setting point, their fluidity is maintained by stirring, and setting occurs as soon as stirring ceases. Syneresis (syrup separation) is much reduced.

5.3.2 Testing Pectins

The various pectins are manufactured with good control of product quality, but variation between manufacturers can occur. In Chapter 15, Tables 15.5 and 15.6 list various types of pectin and each has a particular strength or “grade”. The grade is measured by determining the strength of a jelly made by using a standard formula.

The internationally accepted method to determine pectin gel strength is the Cox and Higby “Ridgelimeter” method. It measures the loss of height or sag of an unsupported jelly. The result is then converted to “grade’ by referring to a graph. Grade is defined as the number of grams of sugar per gram of pectin in a 65% pure water solution at optimum pH that can produce a gel of standard strength. The grade is given the description SAG. A 150 SAG pectin means 1 g of pectin can hold 150 g of sugar at a refractometer reading of 65% Brix and a pH of 2.25–2.45. Most powdered pectin is standardized to 150 grade.

5.4 Gums

Gums are polysaccharides characterized by their ability to give highly viscous solutions at low concentrations. The confectionery industry uses a number of gums; among them are agar, alginates, carageenen, gum arabic (gum acacia), gum tragacanth, guar gum, and locust bean (carob) gum. They are used in candies as stabilizers, thickeners and as extenders in starch and pectin jellies. Gum gels contain in general only about 0.5–1.0% gum; the rest is water. Thus, they are powerful gelling agents. Their use is often limited by the availability and cost of the gum. All gums are tasteless, odorless and colorless.

Gums do not form true solution, but rather, because of their large molecular size and molecular interactions, they form molecular dispersions. The term hydrocolloid is sometimes used interchangeably with gum, although hydrocolloid is a broader term that includes polysaccharides and proteins that serve as thickening or gelling agents. Thus starch, pectin and gelatin are also hydrocolloids.

Gum solutions usually exhibit non-Newtonian pseudoplastic (shear thinning), and occasionally thixotropic (time dependent) flow properties (see Section 15.8.3 for more discussion on non-Newtonian rheology). There are a number of factors that affect their rheological properties,

Table 5.17 Variation of agars of different origin

Agar	Strength[a]	Melt point[b] (°C)	Setting temperature[b] (°C)	Ash (%)	Acid insoluble ash (%)
Japanese	260–310	89–93	33–34	2.3–3.6	0.02–0.3
New Zealand	610–625	90–92	35–36	0.9–1.2	0.06–0.2
South Africa	243–305	86–88	36–36.5	2.3–3.0	0.1–0.2

[a] Bloom gelometer reading on 2% gel
[b] Of 2% gel

including molecular size and weight, concentration, temperature, pH, and presence of other solutes. The same factors also affect their dispersion. The main gums used in candies are briefly discussed below.

5.4.1 Agar: Agar

The name is of Eastern origin and refers to seaweed. In practice, it is simply referred to as agar. It was first extracted from a red seaweed known as *Gelideum.* Because of limited supply, other sources have been investigated. Satisfactory agars have been produced from other seaweeds, including *Gigartina, Gracilaris, Furcellaria and Chondrus.* These seaweeds come from Australia, New Zealand, South Africa. Denmark, Spain, and Morocco. Agar is extracted from the seaweed by boiling and filtering followed by extruding into strips. The strips can be used directly; however, powdered agar is available and preferred because it needs very little soaking before dissolving. Agar varies with its origin. Variations of agars from different origin are given in Table 5.17.

Agar is soluble in boiling water, but insoluble in cold water. The chemical constituents of agar vary with its origin. Agar is basically the sulfuric ester of a long-chain galactan. It consists of a mixture of two polysaccharides, agarose and agaropectin. Agarose is a neutral polysaccharide with little or no ester sulfate groups while agaropectin contains 5–10% sulfate groups. Agarose consists of a linear chain of agarobiose disaccharide units alternating 1–4 linked, 3,6- anhydro-L-galactose units and 1–3 linked D-galactose units. The structure is shown in Figure 5.15.

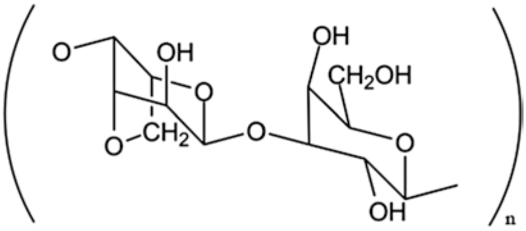

Figure 5.15 Structure of agarose

Agaropectin is a sulfated molecule composed of agarose and ester sulfate D-glucuronic acid, and small amounts of pyruvic acid.

5.4.2 Alginates

The seaweed *Macrocystis pyrifera* is the source of alginates. The seaweed grows off the California coast and can be harvested mechanically. The plant is a perennial and can be harvested continuously. If not harvested, it will break away and float onto the beaches where it can become a great nuisance. The seaweed is processed by washing and milling followed by treatment with hot alkali solution. After clarification, calcium chloride is added to precipitate calcium alginate. After separation the calcium alginate is treated with acid to produce alginic acid. Further treatment with sodium carbonate produces sodium alginate, the most common form of alginates. Alginic acid is a mixed polymer of anhydro-1–4-β-D-mannuronc acid and L-gluronic acid. The structure of alginic acid is shown in Figure 5.16. Alginic acid and its salts of sodium, potassium, ammonium, and calcium are available commercially.

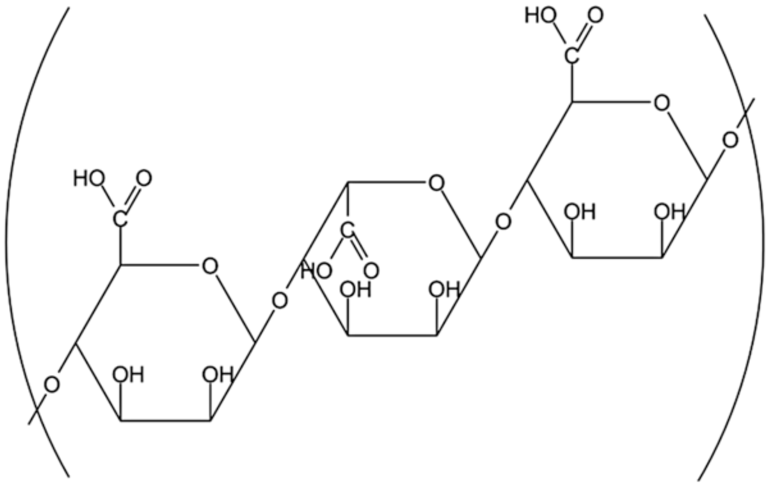

Figure 5.16 Structure of alginic acid

5.4.3 Carrageenan (Irish Moss)

Carrageenan is obtained from the seaweeds *Chodrus crispus* and *Gigartina stallata.* Chemically, it resembles agar and may be classified as a straight chain polysaccharide. Three fractions of carrageenan have been isolated. They are referred to as κ, λ, and ι-carrageenan. κ-carrageenan is made up of 1,3 linked galactose-4-sulfate units and 1,4 linked 3,6-anhydro-D-galactose units. λ-carrageenan consists of 1,3 linked galactose 2-sulfate and 1,4 linked galactose 2,6 disulfate. Approximately 30% of the 1,3 galactose units are not sulfated. The 6-sulfate group can be removed by alkaline treatment in λ as well as in κ-carrageenan. ι-carrageenan consists of 1,3 linked galactose 4-sulfate and 1,4 linked 3,6-anhydro-D-galactose 2-sulfate units. Agar, a member of the carrageenan family, contains little or no sulfate esters while κ, ι, and λ-carrageenan are sulfated in increasing order κ-(approx. 25%), ι-(approx. 30%) and λ- (approx. 35%). None of these polymers contain exact repeating structures.

Among these closely related gums, agar is the least soluble while λ-carrageenan is the most soluble. Agar forms the strongest gel, while λ-carrageenan does not gel. Commercial carrageenan gums contain all three polymers. The composition of polymers will vary depending on source, growth condition, and method of preparation.

Another related gum is furcellaran or Danish agar. It is mainly used in Europe. The properties of Danish agar gels lie between those of agar and κ-carrageenan gels. Furcellaran forms a weak gel in the presence of calcium. It is often used in combination with locust bean gum to achieve greater gel strength.

5.4.4 Gum Arabic

The exudation from the bark of the acacia tree is known as gum arabic. It is also referred to as gum acacia or acacia gum. There are a number of varieties of acacia trees that grow across the African continent. The trees are tapped from incisions made in the trunk and the "tears," which are first soft with a dry skin, eventually dry to a solid lumps. The lumps vary in color from pale amber to reddish shades. Gum arabic is graded by its color. The very pale shades command the highest price. The color differences are due to the presence of tannins, and therefore the darker gums usually have an unpleasant flavor. The lots of lumps are cleaned, and powdered into varying mesh sizes. The highest grade gum is produced by spray drying a clarified solution.

Gum arabic is a heterogeneous material consisting of two fractions. One, which accounts for about 70% of the gum, is a polysaccharide chain while the other consists of acidic protein-polysaccharide. The polysaccharide structures are highly branched arabinogalactans and consist of calcium, magnesium and potassium salts of D-glucuronic acid, D-glactose, D-rhamnose, and D-arabinose. The composition and structure varies with species, season, and climate. Its high solubility in water (40% at 24 °C, 75 °F) and low viscosity is unique among gums. Most gums form highly viscous solution at 1–2% concentration; however, a 20% gum arabic solution has the body of a thin sugar solution. The pH of a 40–50% solution ranges between 4.5 and 5.5. Maximum viscosity is obtained at pH 6.0–7.0. The high solubility and low viscosity are of great value in stabilizing emulsions and holding together solids in pastes. For the same reasons, gum arabic can be used as a polishing agent. The viscosity is retained over a wide pH range and in the presence of other gums and ingredients. In the confectionery industry, gum arabic is used as a binder in lozenges, as a glaze, and as a stabilizer to control crystallization.

5.4.5 Gum Tragacanth

Various species of the thorny shrubs known as *Astragalus* are the source of gum tragacanth. They grow in the semidesert areas of Turkey, Iran, Syria, and India. To harvest the gum an incision is made near the root of the shrub, which is held open by a wedge. The gum exudes in the shape of the incision, a narrow slit produces flakes that dry quickly and are clean and white.

Gum tragacanth contains two polysaccharides. One (60–70%) is known as tragacanth acid or bassorin. The acid swells in water forming a gel. Tragacanth acid contains D-galactose, D-xylose, L-fucose and D-galacturonic acid and a covalently bond protein. The minor polysaccharide is a neutral arabinogalactan in which arabinose is the predominant monosaccharide.

Besides tragacanth forming a gel, an important physical property is its relative acid stability. The gum solution should have a pH of 5.0–6.0, but maximum viscosities are obtained under slightly alkaline conditions. It should not be mixed with gum arabic as under certain conditions it will precipitate. The solid gum should not be stored for long periods because its solubility decreases with age. Gum tragacanth has its main use in candies as binder (mucilage) in lozenge paste. It is often used in combination with gelatin.

5.4.6 Guar Gum

Guar gum is derived from the ground endosperm of seed of the guar plant (*Cyamopsis tetragonolopa)*. The plant, which reaches up to 6 ft in height, is grown in India. The purified gum is extracted from the endosperm of the seed after removal of the husk and germ. The endosperm is practically all gum. Guar gum contains 80–85% guaran, 10–14% moisture, 3–5% protein, 1–2% fiber, 0.5–1.0 ash, and 0.4–1.0% lipid. The polysaccharide of guar gum consists of D -galactose and D - mannose and is therefore a galactomannan. Guar gum is not often used in confectionery applications although it may be used as an extender in starch, agar or pectin jellies, where is can help prevent syneresis, splitting and shrinkage.

5.4.6.1 Locust Bean (Carob) Gum

Locust bean gum is ground endosperm from the locust bean tree (*Ceratonia siligna)*, which grows in the Mediterranean area. The tree grows very slowly and does not produce seeds until at least 15 years old, which limits the supply. The yield of gum from the beans is small, about 3–4%, which further adds to the cost. Like guar gum, it too is a galactomannan. The gum usually contains 80–85% galactomannan, 10–13% moisture, with the remainder made up of protein (~5%), lipid (~2%), fiber (~1%), and ash (~1%). In agar jellies, 0.1–0.2% may be replaced with locust bean (carob) gum. The combination of the two gums results in increased rigidity and prevention of syneresis.

5.4.6.2 Xanthan Gum

Xanthan gum is a high-molecular weight polysaccharide produced during controlled aerobic fermentation of sugars with the microorganism *Xanthomonas campestris.* After fermentation, xanthan gum is precipitated from the fermentation broth with isopropyl alcohol and dried. Xanthan gum is used as a stabilizer and suspending agent in liquids, pastes, and syrups. In confectionery technology, xanthan gum has found limited application. However, in combination with guar and locust bean (carob) gums, it gives increased viscosity, which is beneficial in fillings.

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6 Other Ingredients

6.1 Colors

Color refers to human perception of colored materials. Of the three quality attributes perceived by the consumer, color might indeed be the most important one. A food may be most nutritious, safe, and economical, but if it is not also visually attractive, it will not sell.

A colorant is any chemical, natural or synthetic, that imparts color. Foods are colored by either dyes or pigments. Dyes are chemicals that dissolve in water and lend color to the confection. Dyes absorb light of specific wavelengths, allowing only certain wavelengths of light to pass through the solution, resulting in the unique color. Pigments are insoluble substances that impart color by selectively absorbing certain wavelengths of light and reflecting the remaining wavelengths. Lakes are the only type of pigments allowed in confections.

In the United States food industry, all dyes must be certified by the U.S. Food and Drug Administration (FDA). As such, they are referred to as certified colors, and each is assigned a food, drug and cosmetic (FD&C) number. The FD&C designation means that the dye may be used in foods, drugs, and cosmetics. In addition to the certified colors, certain lakes of FD&C colors are permitted for use. Lakes are made by adsorbing dye molecules on a substratum, which makes the dye oil-dispersible. The dye/substratum combination is achieved either by adsorption, co-precipitation, or chemical reaction. The complex involves the salt of a water-soluble dye and an approved insoluble base stratum. Alumina is the only approved substratum for preparing FD&C lakes. Colorants exempt from certification may also be used. These are natural pigments or synthesized pigments, but nature identical. Lakes must also be certified by FDA, meaning that a batch of dyes must be certified twice to be used in lake form, once as the dye and once again as the lake.

Classification of colorants and an example of each class is given in Table 6.1 (Schwartz et al. 2008).

6.1.1 Regulatory Aspects

Colors allowed in foods are strictly controlled. However, each country has different regulations.

6.1.1.1 United States

In the United States, the use of colorants is regulated under the 1960 Color Additive Amendment to the U.S. Food, Drug and Cosmetic Act of 1938. The amendment classifies colorants, as stated above, into two categories: certified colors and color exempt from certification. Certified colors are synthetic dyes that are not found in nature. Certification means that the dyes meet specific government quality standards. Samples of each batch of colorant are submitted to the

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FDA laboratory for determination of compliance with the established quality standards. Certified dyes are further classified as either permanently or provisionally listed. A provisionally listed dye can legally be used pending completion of all scientific investigation needed to determine for, or against, permanent approval. All seven certified dyes are permanently listed whereas the lakes are provisionally listed with the exception of Red #3, which cannot be used in lake form (Table 6.2).

The color additive amendment includes a simplified nomenclature for certified dyes. Rather than using long common names, certified dyes are referred to by a number and the abbreviation FD&C, D&C, or Ext. (external) D&C. FD&C designated dyes may be used in foods, drugs, or cosmetics; D&C and Ext. D&C dyes can be used only in drugs and cosmetics. The current list of permitted certified dyes contains seven colorants (Table 6.2) along with their regulatory status, their common and abbreviated names, and their E-Numbers (Number listed in the European Community). Today's food regulations mandate the listing of certified dyes by their abbreviated names.

Table 6.1 Classification of colorants

Colorant	Example
Certified	
Dyes	FD&C Blue No. 1
Lakes	Blue No. 1 lake
Exempt from certification	
Natural pigments	Betalains (beet juice concentrate)
Synthetic (nature identical)	β-carotene

Colors exempt from certification must also be declared, but they can be listed generically as "artificial color" or any other specific or generic name for the colorant. The use of the term "natural" is prohibited. Colors currently exempt from certification are listed in Table 6.3. There has been a growing interest in utilizing these natural colors in confections (Lauro and Francis 2000; Jelavich 2016).

6.1.1.2 International

Colors are added to foods all over the world, but the colors permitted vary greatly among countries. Since international trade is becoming increasingly more important, color legislation is of international concern. Unfortunately, a worldwide list of permitted colors does not exist. In the U.S. for example, FD&C Red No.40 is permitted for food use, whereas FD&C Red No.2 was delisted in 1976, but is still in use in the European Economic Community (EEC). Norway, on the other hand, prohibits the use of any synthetic dye in the manufacturing of foods. The EEC has attempted to establish uniform color additive legislation. Each permitted color additive has been assigned an E-Number (E=Europe). The E-numbers for the FD&C dyes are listed in Table 6.2. An abbreviated list of synthetic dyes and natural pigments permitted in the EEC is

Table 6.2 Certified color additives permitted for general use, their corresponding common name and their European Economic Community E-number

			Abbreviated		
FD&C name	Dye	Lake	Common name	Name	E-number[a]
Blue no. 1	Perm.[b]	Prov.[c]	Brilliant blue	Blue 1	E-133
Blue no. 2	Perm.	Prov.	Indigotine	Blue 2	E-132
Green no. 3	Perm.	Prov.	Fast green	Green 3	Not listed
Red no. 3	Perm	–[d]	Erythrosine	Red 3	E-123
Red no. 40	Perm.	Prov.	Allura red	Red 40	E-129
Yellow no. 5	Perm.	Prov.	Tartrazine	Yellow 5	E-102
Yellow no. 6	Perm.	Prov.	Sunset Yellow	Yellow 6	E-110

[a] E-numbers: listed in the European Economic Community
[b] Permanent
[c] Provisional
[d] Use of lake FD&C red no. 3 was terminated effective January 29, 1990

Table 6.3 United States color additives exempt from certification

Color	Use limitation
Annatto	None
Dehydrated beet (beet powder)	None
Canthaxanthin	Not to exceed 66 mg/kg solid food
β-Apo-8′-carotenal	Not to exceed 15 mg/lb of food
β-Carotene	None
Caramel	No restriction unless by proposition 65[a]
Cochineal extract (carmine)	None
Fruit juice/ concentrate	None
Vegetable juice/ concentrate	None
Carrot oil	None
Paprika	None
Paprika oleoresin	None
Riboflavin	None
Saffron	None
Titanium dioxide	Not to exceed 1% by weight of food
Turmeric	None
Turmeric oleoresin	None
Pearlescent pigment[b]	1.25% by weight in cereals, confections and frostings, gelatin desserts, hard and soft candies (including lozenges), nutritional supplement tablets and gelatin capsules, and chewing gum

[a] Caramel has a restriction for the amount of 4-Methylimidazole (4-MeI), a compound produced in caramel manufacture, in California. A level of 29 μg per day is the "No Significant Risk Level" intake

[b] Mica platelet coated with titanium dioxide of different thickness to provide colorant effect

given in Table 6.4. It must be pointed out that use of these colorants may not be permitted in every common market country. The EEC, in addition to the colors listed in Table 6.4, permits the use of chlorophyll, the copper complex of chlorophyll and carbon black. These additional colorants are also permitted in Canada and Japan.

The Food and Agriculture Organization (FAO) and the World Health Organization (WHO) of the United Nations has attempted to harmonize food regulations including color additives through their Codex Alimentarius. This worldwide effort to establish safe use of colorants should lead to internationally accepted regulations for colorant use in foods including candies.

6.1.2 Properties of Certified Dyes

Certified dyes have received increased public attention in recent years. Some of the concern can be traced back to the original term "coal-tar" dyes. Coal tar is perceived as a thick black substance unsuitable for use in foods. The fact is the raw materials for the synthesized certified dyes are highly purified substances that carry no resemblance to coal tar.

Certified dyes fall into four basic chemical classes: azo, triphenylmethane, xanthene, or indigo-type dyes. Listed in Table 6.5 are the FD&C dyes, their chemical class and some of their properties. Listed in Table 6.6 are solubility and stability data for EEC dyes.

Each manufactured dye must meet certain specifications of purity given for certification in the United States Code of Federal Regulations (Title 21, Part 70–83). The color industry not only meets these purity specifications, but most often exceeds them. The dye content of a typical certified dye is 86–95%. The moisture content of a dry dye powder is approximately 4–5% and the ash content is approximately 5%. The high ash content comes from the salt used to crystallize (salt out) the colorant. Although technically these salts could be removed, such steps would be costly and would have minimum benefits.

All water-soluble FD&C azo dyes are acidic, and their physical properties are quite similar. Chemically, they are reduced easily by strong reducing agents and therefore, are susceptible to oxidizing agents. FD&C triphenylmethane dyes (Green 3 and Blue 1) are similar in structure and only differ in one -OH group; therefore, differences in solubility and stability are minor.

Red 3, or erythrosine, is the only xanthene-type dye. Red 3 is insoluble in acid, quite stable to alkali, and exhibits fluorescence. The lake of Red 3 is no longer permitted for use in foods because of toxicologic concerns. Although the

Table 6.4 Synthetic color additives currently permitted in the European Economic Community (EEC) (as of 2016)

Name	E-number	Regulatory legal status[a,b]			
		EEC	US	Canada	Japan
Erythrosine	E-127	+	+	+	+
Brilliant blue	E-133	–[c]	+	+	+
Indigotine	E-132	+	+	+	+
Tartrazine	E-102	+[d]	+	+	+
Quinoline yellow	E-104	+[c]	–	–	–
Yellow 2G	E-107	+[f]	–	–	–
Ponceau 4R	E-124	+[d]	–	–	+
Carmosine	E-122	+[d,e,g]	–	–	–
Amaranth	E-123	+[d]	–	+	–
Red 2G	E-128	+[f]	–	–	–
Patent blue	E-131	+[c]	–	–	–
Green S	E-142	+[d,e,g]	–	–	–
Brown FK	E-154	+[f]	–	–	–
Chocolate brown HT	E-155	+[h]	–	–	–
Black PN	E-151	+[d, e]	–	–	–

[a] + permitted for food use (limited in some countries; – prohibited for food use

[b] No synthetic colors permitted in Norway

[c] Permitted in Denmark, Ireland and The Netherlands

[d] Not permitted in Finland

[e] Not permitted in Portugal

[f] Permitted in Ireland only

[g] Not permitted in Sweden

[h] Permitted in Ireland and The Netherlands

dye is permanently listed, its long-term future is questionable.

Blue 2 is the only indigoid-type dye. It is made from indigo, one of the oldest known and most extensively utilized natural pigments. It is extracted from various indigo plants found in India. Today, Blue 2 is synthesized. The color is a deep blue compared to the greenish-blue of Blue 1. The dye has a low water solubility and the poorest light resistance of any of the FD&C dyes, but it is relatively resistant to reducing agents.

Conditions most likely to cause discoloration or precipitation of certified dyes are the exposure to reducing agents, heavy metals, exposure to light, excessive heat or exposure to acid or alkali. Reducing agents are most troublesome. Common reducing agents are monosaccharides (glucose and fructose), aldehydes, ketones, and ascorbic acid. Free metals can react chemically with many dyes causing loss of color. Of most concern are iron and copper. The presence of calcium and/or magnesium can result in the formation of insoluble salts and precipitates.

6.1.2.1 Use of Certified Dyes

Uniformity is achieved in incorporating a water-soluble dye into a food if the dye is first dissolved in distilled water. Distilled water must be used to prevent precipitation by minerals in the water. Today, liquid colors with concentrations of 10–15% can be purchased from manufacturers. Citric acid and sodium benzoate are commonly added to prevent spoilage.

Many candies are low in moisture, sometimes making it difficult to completely dissolve and uniformly distribute a dye, resulting in weak color and/or speckling effect. This is a potential problem in, for example, hard candies, which typically have a moisture content of less than 3% and where the color is most often added after cooking to that final water content. The problem can be overcome by the use of solvents other than water, such as glycerol or propylene glycol (Table 6.5). Pre-dispersion of a dye in these solvents helps prevent agglomeration of particles, and thereby helps develop full color intensity and reduce or prevent incidence of speckled product.

Table 6.5 Certified colorants and their chemical and physical properties

Common name and FD&C number	Solubility (g/100 ml)[a] at 25 °C					Stability[b]								
	Dye type	Water	Propylene glycol	Alcohol	Glycerine	At pH				Light	10% AcOH	250 ppm SO_2	1% ascorbic acid	1% sodium benzoate
						3.0	5.0	7.0	8.0					
Brilliant blue Blue no. 1	Triphenyl-methane	20.0	20.0	0.35	20.0	4	5	5	5	3	5	5	4	6
Indigotine Blue no. 2	Indigo	1.6	0.1	In	20.0	3	3	2	1	1	1	1	2	4
Fast green Green no 3	Triphenyl-methane	20.0	20.0	0.01	1.0	4	4	4	4[b]	3	5	5	4	6
Erythrosine Red no. 3	Xanthine	9.0	20.0	In	20.0	In	In	6	6	2	In	In	In	6
Allura red Red no. 40	Azo	22.0	1.5	0.001	3.0	6	6	6	6	5	5	6	6	6
Tartrazine Yellow no. 5	Azo	20.0	7.0	In	18.0	6	6	6	6	5	5	3	3	6
Sunset yellow	Azo	19.0	2.2	In	20.0	6	6	6	6	3	5	3	2	6

b1 = hue turns blue; b2 = hue turns yellow

[a] In, insoluble

[b] 1 = fades; 2 = considerable fade; 3 = appreciable fade; 4 = slight fade; 5 = very slight fade; 6 = no change

Table 6.6 Chemical and physical properties of common European Economic Community (EEC) dyes

	Solubility (g/100 ml) at 16 °C				Stability[a/]				
								pH	
Name and EEC number	Water	Propylene glycol	Alcohol	Glycerine	Light	Heat	SO_2	3.5/4.0	8.0/9.0
Quinoline yellow, E104	14	<0.1	<0.1	<0.1	6	5	4	5	2
Ponceau 4R, E124	30	4	<0.1	0.5	4	5	3	4	1
Carmoisine, E122	8	1	<0.1	2.5	5	5	4	4	3
Amaranth, E123	5	0.4	<0.1	1.5	5	5	3	4	3
Patent blue, E131	6	2	<0.1	3.5	6	5	3	1	2
Green S, E142	5	2	0.2	1.5	3	5	4	4	3
Chocolate brown HT, E155	20	15	Insoluble	5	5	5	3	4	4
Brilliant black BN, E151	5	1	<0.1	<0.5	6	1	1	3	4

[a] 1 = fades; 2 = considerable fade; 3 = appreciable fade; 4 = slight fade; 5 = very slight fade; 6 = no fade

A second approach to overcome the problem of poor dispersion is the use of "lakes". Lakes exist in low moisture candies as dispersions rather than in solutions. Lakes range in dye content from 1% to 40%, with the dye molecule attached to the alumina particle. A high dye content does not necessarily lead to more intense color. Particle size is of great importance – the smaller the particle size, the finer the dispersion and the more intense the color. Special grinding techniques used by color manufacturers have made it possible to prepare lakes with mean particle size of less than 1 μm.

Color manufacturers also prepare color pastes or solid cubes of dyes and lakes. A paste is made with the addition, for example, of glycerol as a solvent and powdered sugar to increase the viscosity. Colorants, in the form of cubes, are achieved by adding gums and emulsifiers to color dispersions in the manufacturing process.

6.1.3 Colors Exempt from Certification

Colors exempt from certification have found growing application in candies based on consumer demand even though the range of colors is different from that obtained with the FD&C dyes. A brief description of the colorant list in Table 6.3 follows.

Annatto is the extract prepared from Annatto seed, *Bixa orellana L.*, through organic solvent extraction. The main pigment in annatto is the carotenoid bixin, which is not water soluble. Norbixin is the water-soluble form. These compounds produce a yellow to golden-orange color and are fairly stable to heat, light and pH. Annatto color is widely used in the dairy industry to color butter and cheese.

Red beet concentrate, classified as a vegetable juice color, is made by concentrating beet juice. The pigments in beet colorants are betalains [betacyanin (red) and betaxanthins (yellow)]. The main betacyanin in beets is betanin and the main betaxanthin is vulgaxanthin. The ratio of betacyanin/betaxanthin varies depending on cultivar and maturity of beets. Controlling the pigment ratio results in different shades of red, from pink to purple. Beet colorant can also be produced under the category of "vegetable juice". This type of beet colorant is obtained by concentrating beet juice under vacuum to a solid content sufficient to prevent spoilage (about 60%). New beet varieties have made it possible to obtain juice concentrates with pigment concentration between 1.5% and 2.0%. It has poor heat and light stability, and works best in the pH range from 3.5 to 5.5.

Canthaxanthin (water soluble) and β-Apo-8′-carotenal (oil soluble) are synthesized carotenoids, regarded as "nature identical". They produce orange-red colors. β-carotene is another carotenoid that can be used as a colorant. It can be either obtained from nature or chemically synthesized and provides yellow-orange-peach colors. These oil-soluble compounds are stable to heat, light and pH, but are susceptible to oxidation.

Caramel color is a dark-brown liquid produced by heat-induced caramelization of carbohydrates, covered by a Standard of Identity (21 CFR Section 73.85). The CFR governs which carbohydrates can be used and whether sulfites or ammonia can be used. With a brown color, caramel colorant provides good heat, light and pH stability. They have found application in sugar free caramel and fudges, among other applications.

Cochineal extract is the concentrate produced from an aqueous-alcohol extract of the cochineal insect, *Dactylopius coccus costa.* The coloring is principally due to carminic acid, a red pigment. The extract contains about 2% carminic acid. Colorants with carminic acid concentration of up to 50% have been produced. These colorants are sold under the name carmine colors and provide a range of color from orange to pink to red shades. The pigment is stable under most processing conditions. They have the disadvantage of being unacceptable for Kosher or Halal products.

Fruit juice and their concentrates are acceptable color additives. Depending on the source of the juice, a number of pigment types can be involved. Pigments found in fruit juices are generally pH sensitive. Red fruit juices most likely contain anthocyanins. These pigments are not very heat stable and are only red at pH values below 4.0. Anthocyanins provide blue to purple color at alkaline pH.

Carrot oil is produced by extracting edible carrots with hexane. The hexane is subsequently removed by vacuum distillation. The pigments in carrot oil are mainly α and β-carotene and other minor carotenoids and, as such, provide yellow-orange colors.

Paprika or paprika oleoresin is either the ground, dried pods of paprika (*Capsicum annuum L.)* or an extract of the plant, obtained by organic solvent extraction. The main pigment in paprika is capxanthin, a carotenoid, although other carotenoids are present as well. Paprika gives an orange-red color. The colorant is naturally oil soluble but water-soluble forms are available in either emulsion or spray-dried powders. It has good overall stability to heat, light and pH, but oxidizes readily.

Riboflavin or vitamin B_2 is an orange – yellow powder available as a powdered pigment or as a dispersion. It has been produced commercially by chemical synthesis, by fermentation or by a combination of chemical synthesis and fermentation. Fermentation is the most cost-effective process and is now used widely. Riboflavin has decent heat stability but poor light stability and a distinct flavor off-note.

Saffron is the dried stigma of *Crocus sativul L.* Its yellow color is attributed to the pigment croxin. A water-soluble colorant that comes as either a solution or a powder, it is stable to heat, light and pH. At more than $500 per pound, its cost generally precludes it from commercial application.

Turmeric and turmeric oleoresin are the ground rhizomes or an organic solvent extract of turmeric (*Curcuma longa L*). The coloring matter in turmeric is curcumin, providing a yellow shade. It has excellent heat, good pH stability below pH 6.5 but poor light stability. At pH >6.5, it turns orange.

Spirulina blue is obtained as a water-soluble extract from Spirulina algae. The colorant is phycocyanin, which can give a color from pale blue to violet blue. It has fair heat stability, poor to fair light stability, with a pH range of 4.0–7.0.

Chlorophyll (oil soluble) and chlorophyllin (water soluble) are green colorants found in many plants and algae. Although not approved for use in the United States, they are allowed in other parts of the world. They have very good heat and light stability, and provide desirable colors over a wide pH range.

Iron oxides are now permitted for use in gum and confections in the United States. Although there are numerous oxides in nature (rust is a natural iron oxide), the most common colorants are red, yellow and black iron oxides. These can be blended to provide a wide spectrum of colors, including “earthy” oranges, browns and greens. They are quite stable, almost inert.

Titanium dioxide is the only white colorant permitted (21 CFR Section 73.575) in the United States. It is a mineral (rutile or anatase) particulate that acts as a dispersed pigment in confections. Being a mineral, it is extremely inert to heat and light, and can be dispersed in both water and oil. It is often used to provide opacity and blends with other colors to give pastels. Its use is limited to 1% in the United States. There are some new whitening agents being produced and used in the food and confectionery industry with good success. These contain a mixture of starches and gums that can provide the same whitening/opacifying result of titanium dioxide. A higher usage rate is needed to achieve the same or similar whitening effect as titanium dioxide, with a slightly higher cost. These new whiteners have performed well in panning, gummies, hard candy, and licorice applications. Note that calcium carbonate cannot be used as a color additive in the United States.

6.1.3.1 Use of Colors Exempt from Certification

With the exception of synthetic, nature identical pigments, colorants exempt from certification are chemically crude preparations. They are either juices, concentrate juices or extracts that have undergone little or no purification. The pigment concentrations are relatively low, and to obtain the desired color larger amounts are required. This has caused some to suggest that the pigments lack tinctorial strength and contribute to undesirable flavors to the product. Neither criticism is necessarily true. Many pure natural pigments have high tinctorial strengths with little or no off-flavor notes.

When switching from synthetic to exempt colors, certain problems arise. These relate to stability issues with the different color sources, introduction of off-flavors from the color, the availability of certain shades to match the synthetic dye colors, and cost. Many exempt colors are more expensive than synthetic.

Some general guidelines for introduction of exempt colors into confections are as follows. In candies that are cooked to high temperatures, exempt colors must be added after cooking is completed to ensure that heat-sensitive colorants retain their intended shade. It must be ensured that the exempt colors are uniformly dispersed throughout the candy mass. The pH of the candy must match the desired shade for many exempt colors. Packaging must be sufficient to protect those colors that are light sensitive. Finally, the choice of water-soluble or oil-soluble color depends on the confection, with compound coatings being the primary application for oil-soluble colors.

6.2 Flavor and Flavoring Materials

Whatever food we consume, it is judged by three quality attributes: color, flavor, and texture. Within the limits of choice, which may be impacted by availability and cost, the consumer will select those products that give the most pleasure. It is unlikely that the consumer would select a product that looks unattractive, has an objectionable odor, or has an undesirable texture. It is difficult to determine which of these three quality attributes is most important in the consumer making a choice, but certainly flavor has a significant impact on the product selection.

Flavor preference and acceptance/rejection of foods, including confections, display great variability, and depend on a number of factors including ethnic origin, education, age, upbringing, and the environment. A candy acceptable to one consumer may be rejected by another. Psychological factors may also be involved. The challenge is to find the right balance of acceptable attributes that determine the commercial success of any product.

Flavor is a complex sensation induced by chemical compounds present in the foods we eat or drink. It may be more accurately defined as the simultaneous appreciation of stimuli on the receptors of tastes on the tongue, and smell in the nasal cavity, and of the feeling and temperature receptors located throughout the mouth and throat. The stimuli produced by the smell and the sensations in the mouth, give rise to microelectrical impulses that pass from the specific receptors to definite locations in the brain, where they are translated into recognizable experiences. Flavor has been defined by the International Organization of Standards (ISO) as the "Complex combination of the olfactory, gustatory, and trigeminal sensations perceived during tasting. The flavor may be influenced by tactile, thermal, painful and/or kinesthetic effects." (ISO 5492, 2008).

The first impression the consumer has of any food product is appearance, which includes color. This has a direct impact as visual attractiveness makes one product different from another. The consumer tends to select products according to color and anticipated flavor. He or she expects a red colored candy to have a strawberry, cherry or raspberry flavor, similarly an orange color is associated with a citrus fruit flavor. Appearance is a valuable attribute right to the point of ingestion. At the time of eating, the volatile components in some products may be inhaled through the nose, thereby stimulating the olfactory receptors; this effect is fortified as the volatiles are released in the mouth during chewing and swallowing. At this time, the basic taste factors and other superficial stimuli are appreciated so that the full flavor is recognized. It is at this point that the full pleasurable or unpleasurable response is made and the product judged acceptable or unacceptable.

Flavors play numerous roles in confections, and indeed in all foods. They should provide a pleasant taste sensation that matches the color of the confection. They should supplement, enhance or modify the taste profile for a confection. As seen with the continuous development of new and unique flavor sensations, they should provide novelty and innovation. Flavors may be used to replace an ingredient or compensate for a reduction of an ingredient. In some cases, they may be used to mask off flavors from other ingredients.

The subject of flavor is by no means simple and numerous unrelated factors have to be taken into account. Regional preferences can significantly influence product acceptance. For example, dark chocolate is preferred in most European countries, while milk chocolate is preferred in the United States. The after-dinner mint, widely liked in England, took years to find acceptance in the United States.

6.2.1 Sources of Flavors

Candies differ from the majority of other foods in that the major ingredient is sugar or sugar substitutes. Apart from the intrinsic sweetness, sugar and sugar substitutes have no other flavors and hence, the flavor of the finished candy must be achieved by the addition of flavoring materials. In selecting a flavor, many variables must be taken into account and therefore, it is often difficult to generalize. Factors to consider are method of manufacturing, marketing requirements, and consumer acceptability. Flavorings may be natural in composition, they may be synthetic compounds, or they may be a blend of both. Whatever the formulation, the end product must produce a flavor that has the maximum level of acceptance. In achieving this, all flavorings must satisfy the following criteria:

1. It must be harmless in use and present no health hazard,
2. It must fit the end product technologically and in keeping with the product concept,
3. It must comply with all legislative requirements in force in the country in which the product is offered for sale,
4. It should be convenient to handle, capable of accurate dosage, and readily incorporated into the product mix, giving a uniformly dispersed flavor,
5. It must be stable before, during and after incorporation into the final product,
6. It must resist adverse storage conditions, and
7. It must be economically viable for both the flavor manufacturer and the candy manufacture.

In terms of labeling, there are several types of flavor categories according to the FDA in the United States. These include artificial flavors, natural and artificial flavors, natural type flavors, natural flavors, and natural flavor WONF. Artificial flavors are those where the predominant flavor comes from artificial ingredients. A synthetic strawberry flavor would be an example. Natural and artificial flavors must contain a natural source of the flavor but may also contain artificial flavoring materials. This might be some strawberry concentrate along with the synthetic flavor. Natural-type flavors are natural flavors that do not contain the named ingredient. A natural-type strawberry flavor would contain natural ingredients, but no actual strawberry component. Natural flavors must contain a natural source and be all natural. A natural strawberry flavor must contain a natural source of strawberry with no other flavors added to enhance that flavor. The final category is natural flavor WONF (with other natural flavors). Here, additional natural flavors could be added to the strawberry flavor source. Addition of natural flavor components can greatly enhance the flavor experience from natural ingredients.

6.2.2 Flavor Balance

Many flavors used in candy are based on familiar fruits (e.g., raspberry strawberry, grapes, citrus fruits). Unfortunately, the natural flavors in these fruits occur in relatively low concentrations, which therefore makes them a poor source of flavor concentrates for use in confections. As a consequence, many flavorings used in candies are synthetic flavors that may be identical to those present in the natural fruit. Such flavors generally have a very close profile to that found in nature and can be formulated to give almost any desired aromatic nuance. However, consumers are requesting more natural ingredients, spurring a push to the use of more natural flavors in confections.

Most fruits are characterized by the presence of a fruit acid (e.g., citric, malic, tartaric). Without these acids, the flavor would be incomplete and either extremely sweet or unpleasantly flat. To achieve an acceptable fruit flavor, it is necessary to pay attention to the sugar/acid ratio balance appropriate for the flavor type. The average sugar/acid (citric) ratio for cherries, raspberries and strawberries are 9.2, 2.1, and 6.1, respectively and for apples the sugar/acid (malic) ratio is 1.4. For this reason, many fruit-based confections also contain an organic acid (or two) to enhance the natural flavor. Generally, the acid most prevalent in the fruit is the most desirable acid to complement the fruit flavor.

6.2.3 Flavor Sensation

The primary flavor sensations are taste, detected through stimulation of taste receptors in the body, and aroma (odor), through detection in the nasal cavity. Stimulus of the trigeminal nerve also influences our sense of flavor perception. Although not contributing directly to the molecular flavor perception, texture (tactile), visual sensations, thermal effect, and other hedonic factors also contribute to the acceptability of a product.

Genetic, physical and psychological differences among individuals generally account for the differences in flavor perception. Beyond the genetic differences that lead to varied perception among individuals, difference in the shape of an individual’s oral cavity and the chewing pattern also affect release of flavorant molecules. Psychological factors also play a role. For example, some studies have shown that the color and even shape of the plate from which we eat a food can influence our sensory perception. Customs (e.g., what you grew up with) and other ingrown “biases” (e.g., higher cost products must taste better) also influence our flavor sensation. Flavor perception is indeed complex.

6.2.3.1 Taste

Taste is detected through the contact of certain water-soluble, mostly nonvolatile compounds dissolved in the saliva with the taste buds on the tongue. It is widely accepted that there are five basic taste sensations: sour, sweet, bitter, salty, and umami. Some suggest that fatty and metallic qualities should also be called basic tastes (Chaudhari and Roper 2010) The perception of these taste sensations occurs mostly in the oral cavity, although taste receptors can actually be found in various places in the body, including the respiratory tract, stomach, intestine, pancreas, liver, kidney and even the brain (Yamamoto and

Ishimura 2013; Depoortere 2014). It is the complex interactions across these receptors that lead to the overall taste of a food product.

When a confection is ingested, numerous processes take place in the oral cavity that release flavorants. These compounds are brought to the taste buds on the tongue through a combination of diffusion and convective processes as saliva dilutes the food matrix. Some of the differences in taste sensations among individuals are due to differences in the oral cavity and the process of mastication among individuals. Such differences may be related to factors related to the mouth (including saliva production, chewing intensity, air flow, etc.) or the food itself (i.e., mechanical properties, rheology, lipophilic/hydrophilic nature, melting point of a fat, etc.). These factors influence the ability of the flavorant to interact with the taste receptors in the mouth.

In the older literature (and some textbooks still), taste buds specific to each sensation (sour, sweet, etc.) were loosely grouped in discrete sections of the tongue. It is widely accepted now that most taste buds provide multiple taste responses (Lindemann 1999), although specific details for taste reception are still the subject of research.

Once a flavorant interacts with a taste receptor, a complex series of biochemical processes takes place that eventually leads to the signal in the brain that denotes a specific flavor. Details of this process are beyond the scope of this book. More details on the biochemistry of taste buds and receptors that lead to transmission of signals to the brain can be found in such references as Lindemann (2001), Chaudhari and Roper (2010), and Roper (2013).

6.2.3.2 Aroma (odor)

Another aspect of flavor sensation is through the olfactory nerve. For a chemical compound to pose an aroma, it must be volatile to enable it to reach the nasal cavity, where the olfactory sensory region is located. Olfactory receptors, in direct contact with air passing through the nose, interact with the volatile aroma molecules released from the food. Transmission of an electric signal from this interaction is mediated by the olfactory nerve, to initiate a response in the brain. However, the precise mechanism enabling humans to recognize and positively identify thousands of different aromas is not very well understood.

Over 10,000 aromas have been identified; some say there are an infinite number of aroma sensations. Sensitivity to aromas is much greater than sensitivity to tastes; only molecular quantities of a substance are necessary for detection. Of course, the intensity of a smell is dependent on the number of aroma molecules interacting with the olfactory receptors. However, continuous exposure to an aroma can lead to the phenomenon of habituation, where we are no longer able to perceive a smell even though it is still pervasive. Aroma perception quickly recovers after the stimulus is removed.

Although the nose is more sensitive than any instrument, it can only detect the overall aromatic profile. In contrast, an instrument (gas chromatography, GC) can separate and detect individual molecular components of an aroma, although it cannot give information on the sensory impact. For the nose to be applied as an analytical "tool" to identify different aromas requires considerable training. In recent years, the electronic nose has become increasingly useful to mimic human olfaction while enabling identification of specific odorants (Loutfi et al. 2015).

6.2.3.3 Trigeminal Sensations

Some aspects of flavor are detected through the trigeminal nerve, particularly those that might be called "irritants". These stimuli include thermal (hot/cold), spicy (peppers), cooling (menthol), caustic (vinegar) and astringent (mouth puckering). These senses may be more or less important in confections.

For example, it is common to find menthol-containing hard candies or lozenges that provide relief from sore throat, or other health issues. When consumed, the menthol is released into the oral cavity, where it stimulates the trigeminal nerve, providing a cooling sensation. Also, the spicy hot sensation from capsaicin arises from stimulation of the trigeminal nerve to produce a specific reaction that is perceived as spicy or hot.

Although these trigeminal responses are not a direct "flavor" sensation, they contribute to overall sensation of taste.

6.2.3.4 Texture (Tactile) and Other Flavor Stimulants

Texture and other flavor stimulants by themselves have no flavor, but they can contribute significantly to the overall acceptability of a product. Besides texture, the flavor of a product is impacted by various parameters including the visual sensation, auditory sensation, thermal effect, and hedonic factors.

Texture is very important to product acceptability, especially in confections. Texture influences the rate at which a flavor is released. When hard candy is enjoyed, it dissolves slowly from the surface inward and the flavorings are continuously released over the entire eating period. In contrast, in soft confections such as fondants, crèmes or chocolates, the entire piece quickly softens in the mouth and the total flavor is released. Simultaneously, the type and quantity of flavorings used must relate to these factors to achieve optimum response.

Other tactile sensations are crispness, crunchiness, and smoothness. Chocolate, which the consumer anticipates to be smooth, if poorly refined (see Chapter 16), will be gritty- a textural characteristic detrimental to chocolate flavor.

6.2.4 Flavoring Materials

Flavor materials are very important ingredients in candy production. The character of most candy products depends entirely on added flavorings. All flavorings are composed of highly aromatic compounds, which are either naturally occurring or are specifically selected to contribute to a particular flavor profile.

6.2.4.1 General Classification

Flavoring materials include (Minifie 1989):

1. Naturally occurring plant materials,
2. Products derived from plant materials by some physical process; e.g., extracts, concentrates, essences, essential oils, and oleoresins,
3. Isolates or pure chemicals prepared from natural products; e.g., eugenol from clove leaf oil or citral from lemon grass oil,
4. Synthetic chemicals, prepared from natural isolates or other natural products; e.g., vanillin from wood lignin,
5. Nature-identical synthetic chemicals,
6. Artificial aromatic chemicals,
7. Flavor enhancers,
8. Taste modifiers; e.g., salt, sugar, and
9. Solvents or carriers.

6.2.4.2 Natural Flavors

Natural flavors are derived from plant sources. They may come from the juice, as purees or as distillates obtained from the peel (or other component). They are generally subjected to some concentration process to increase strength. Depending on the application, the severity of the heat treatment in particular can significantly influence the flavor profile.

6.2.4.2.1 Fruit Flavors

Most fruits contain between 85% and 90% water and must be concentrated if used as a flavoring material. Vacuum concentration is essential to minimize flavor loses. Other potential concentration technologies include freeze drying, reverse osmosis and spray drying. Although these methods preserve much of the flavor, cost must be taken into consideration. Fortified fruit concentrates are largely natural juice concentrates fortified with either an artificial flavor or essential oils that can provide more depth of flavor. The artificial flavors are synthetic flavor compounds identical to those found in the natural fruit. Fruit purees are also used for flavoring purposes.

Fruit flavors are used in a wide range of confections, although the specific flavor profile can vary widely. Fruit concentrates, purees and distillates provide the basic flavor nuance, which is then enhanced to provide unique flavors.

6.2.4.2.2 Essential Oils

Essential oils are also known as volatile oils because they evaporate at room temperature when exposed to air. They are a complex mixture of organic compounds obtained by distillation, expression or solvent extraction from plant material. The botanical source of the oil gives it its name and odor. In Table 6.7, a number of essential oils, their name, origin and main physicochemical parameters are listed. The constants are of significance because small deviations from these values are indicative of poorly purified oil, or may indicate deterioration because of oxidation. The constituents of essential oils are synthesized by the plant during its normal growth. Different parts of the plant impact the composition and aromatic strength. Quality of the essential oil is further influenced by different growing conditions and locations.

The constituents of essential oils are primarily hydrocarbons, terpenes of the general formula $(C_5H_8)_{n.}$ When n = 2, they are called monoterpenes; n = 3 sesquiterpenes; and n = 4, diterpenes. In addition to terpenes, essential oils include alcohols, ketones, phenols, aldehydes, and esters. Essential oils are volatile and because of their low vapor pressure can easily be distilled. Most oils are vacuum distilled, because distillation in air at ordinary pressure involves higher temperatures, and the presence of oxygen results in decomposition. Peppermint, cassia, cinnamon, nutmeg, clove, pimento (allspice), caraway, anise, and rose are all distilled oils used in confections. The essential oils from peels of various citrus fruits are not recovered by distillation, which causes decomposition, but rather by mechanical expression. Only lime oil is recovered as a by-product of lime juice production. Some oil is recovered from citrus waste by distillation, but these oils are of poor quality.

The presence of high concentrations of terpenes has a detrimental effect on the keeping quality of many oils. A better flavor is obtained by using terpeneless oils, but these can be cost prohibitive. These are made by solvent extraction with dilute alcohol. The terpenes separate as an oily layer leaving the flavorful, oxygenated compounds in a clear layer. They are obtained by fractional distillation under vacuum, or by chromatography using silica gel.

Essential oils, because of their complex nature, are very susceptible to deterioration by either loss of volatile components or the development of off-odors due to oxidation. Because of possible oxidation, antioxidants are used.

Off-flavors and off-odors can also be caused by exposure to iron and direct sunlight. For these reasons, it is important that essential oils only be handled in stainless steel containers and only be exposed to stainless steel equipment. It is preferable to store essential oils in well-filled amber colored glass bottles in a cool and dark place to prevent off-flavors and odors.

A number of essential oils are used in the flavoring of confections (Table 6.7). The blends and quantities used are best determined experimentally, because they are affected by other raw materials present and processing conditions.

6.2.4.2.3 Herbs, Spices and Spice Products

Herbs, spices and spice products play a significant role in savory foods, but they have typically has limited application in confections. One exception perhaps is in the artisanal chocolate segment, where their use seems to be growing in popularity. Besides ground herbs and spices, a number of processed spice products are available. They include essential oils, oleoresins, blended seasonings, emulsions and solubilized spices. They may be used in truffles to create unique flavors.

6.2.4.2.4 Other Natural Flavoring Materials

A variety of natural products now find application as flavorings in confections. These include, but are not limited to, coffee and vanilla. Tea and cocoa are also considered natural flavoring materials.

6.2.4.2.4.1 Coffee

Coffee is a very popular flavor in candies and chocolate. Coffee is generally recognized as an acquired taste, and many blends and degree of roasts are available. The connoisseur most likely prefers a high roast strong coffee, but the more popular flavor is a milder light roast coffee. Dried water extracts are most often used to deliver the flavor to candies and chocolate. Freeze dried extracts result in high quality flavors.

Coffee "liquors" are another method of incorporating coffee flavor into confections. Liquors are prepared by grinding freshly roasted beans in

Table 6.7 Origin and main constituents of some essential oils

Essential oil	Origin	Characteristics
Oil of almond	Kernels of bitter almond *Prunus amygdalus*, peach *P. persica*, apricot *P. armenica*	Contains about 97% benzaldehyde
Oil of aniseed	True aniseed *Pimpinella anisum* (Europe)	Contains 80–90% anethole
	Star aniseed *Illicium verum* (China)	
Oil of bay	Leaves of the laurel tree *Pimento acris* and *Laurus noblis*	Contains 50 to 50–70% phenolic compounds
Bay leaves		
Oil of caraway	Distillate from seeds of *Carum carui*	Contains 50–60% carvone, along with D-limonene
Oil of cardamom	Fruit of *Alleppy cardamoms*, *Elettaria cardamomum*; also from *Malabar* and *Mysore cardamoms*	Complex mixture of esters of cineol and terpineol
Oil of cassia	Distillate from the bark, leaves, and twigs of the Chinese cinnamon, *Cinnamonum cassia*	Contains 75–90% cinnamic aldehyde
Cassia bark		
Oil of cinnamon	The under-bark (quills) of the tree *Cinnamonum zeylanicum*	Contains 60–75% cinnamic aldehyde with 5–10% eugenol
Cinnamon bark		
Oil of celery	The celery plant *Apium graveolens*	Contains mainly D-limonene; primary flavor compound is sedanolide
Celery seed		
Oil of cloves	Extract of Zanzibar clove flower *Eugenia caryophylata*	Contains 90% eugenol with associated esters
Oil of coriander	Prepared from the fruit of the Russian coriander *Coriandrum sativum*	Contains about 70% D-linalool
Oil of fennel and fenugreek	Prepared from fruits of *Foeniculum vulgare* and *Trigonella foenum graceum,* respectively	Sweet oil of fennel contains mainly anethol, but also fenchone and dipentene
Oil of ginger	Manufactured from ginger *Zingiber officinale*	Main constituents are dextrocamphene and β-phellandrene
Oil of lemon	Obtained from the peel *Citrus limonum*	Contains 85–90% D-limonene; essential flavor compound is aldehyde citral
Oil of lime	Derived from the peel of the fruits *Citrus limetta* and *Citrus aurantifolio*	Pressed oil contains 6–9% citral; Distilled oil contains 1–10% citral
Oil of Neroli	Distillate from fresh flowers of the bitter orange (sweet oil) *Citrus aurantium amara* and *Citrus bigaradia* (bitter oil)	Primary constituents are linalyl acetate and L-linalol; main odorant is methyl anthranilate
Oil of orange	Oil of sweet orange derived from the tree (sweet oil) *Citru sinensis,* the bitter oil from *Citrus aurantium amara*	Contains 90–95% D-limonene; decaldehyde and nonylacetate give main orange character
Oil of rose, otto, or attar of rose	Distillate of fresh rose petals, *Rose damascena* Otto derived from *Rose alba, moschata and centifolia*	Main compounds are geraniol and isomers plus citronelli and isomers;
Spearmint oil	Distilled from the herb *Mentha virdis*	Contains primarily carvone, phellandrene and L-limonene
Oil of Peppermint	Distillate of the plant *Mentha piperata* or of the plant *Mentha arvensis* (Japanese plant)	Contains 50–65% L-menthol and 9–19% menthone, along with menthyl actetate and iso-valerate

From Minifie (1989)

either vegetable fat or cocoa butter. As with coffee extracts, the selection of beans and the degree of roasts will impact the final flavor.

6.2.4.2.4.2 Vanilla Flavorings

Vanilla flavorings find wide use in candies and chocolates, in part because they enhance other flavors. Natural vanilla is used in high quality confections; the majority of products are flavored with synthetic vanillin and ethyl vanillin.

Natural vanilla is obtained from the pods of a tropical orchid known as *Vanilla planifolia.* The flowers develop over several months into green pods about 15–23 cm (6–9 in.) long. Vanilla is cured similar to cocoa to develop the characteristic flavor. The pods are picked green and steeped for about a month in nut oil until they are fully ripened, at which time they are black. During the curing process, the flavor precursors, which are glucosides, are broken down into vanilla and glucose. The main chemical compound in vanilla is vanillin, which is present at a level of 1.3–3.8%; however, a number of minor aromatic compounds are also produced. These minor compounds significantly contribute to the complex aroma of natural vanilla, which is lacking in the synthetic vanillin product.

Vanilla extract is made by cutting the beans into small pieces and soaking them in successive quantities of hot (65–70%) alcohol. Alcohol extraction is the best method to ensure that a true vanilla flavor is obtained. There are many vanilla extracts on the market that are blends of natural and synthetic compounds.

The manufacturing of synthetic vanillin ($C_6H_3OH{\cdot}OCH_3{\cdot}CHO$) was one of the earliest achievements in flavor chemistry. Vanillin can be produced from the clove oil eugenol or from guaiacol, and is recovered by vacuum distillation. In the past, clove oil vanillin was considered to have the best quality. Today, virtually all vanillin is produced from petrochemicals. The solubility values of vanillin in water, 90% alcohol, 95% isopropyl alcohol, and 50% glycol are 0.5%, 40%, 80%, and 15%, respectively.

In ethyl vanillin ($C_6H_3OH{\cdot}OC_2H_5{\cdot}CHO$), the methyl group has been replaced by an ethyl group. Although originally it was difficult to produce without impurities, today's technology allows for the production of a high quality product that is widely used. Its main advantage is that it is claimed to be five times stronger in flavor compared to vanillin, which gives it an economical advantage. The solubility in water is 0.4% and in 90% alcohol it is 20%. Five percent solution of ethyl vanillin in equal parts of isopropyl alcohol and water is often used for flavoring purposes. Both vanillin and ethyl vanillin are considered to be quite heat stable (compared to vanilla) and are also available in crystalline and powdered forms.

6.2.4.3 Synthetic Flavors

Natural flavoring materials provide a wide range of flavors, and although their use in confections is continually growing, there is still need for synthetic flavors. Synthetic or compounded flavors have the flavor strength, composition, and stability needed in today's processing conditions.

Food regulations control the use of artificial flavors while allowing the use of natural or nature-identical within acceptable limits. Whatever the nature of chemicals used to produce an artificial flavoring, the ultimate purpose is to produce, as closely as possible with the raw materials available or permitted, the odor and flavor effect of the natural flavoring in the end product. Modern analytical instrumentation used in flavor research has resulted in the isolation and characterization of hundreds of organic chemicals responsible for the aromas and flavors of almost all natural flavoring materials.

The preparation of a flavoring material is not a task for the confectionery manufacturer; it should be left to flavor manufacturers who have the knowledge and the facilities to carry out these tasks. The list of flavor materials is comprehensive and there are excellent imitations of most natural flavors. Most flavor manufacturers will readily supply samples and use data applicable to various end products.

6.2.4.4 Solvents and Carriers

Appropriate permitted solvents or carriers often provide a vehicle to deliver the flavor to the confection. Common solvents include water, alcohol, ethyl glycol, propylene glycol, and vegetable oils. Choice of solvent depends to a great extent on the nature of the flavor, whether hydrophilic or hydrophobic, and final product end use. Generally oil-based flavorings are used in fat-based confections (such as chocolates and melt-aways) to prevent thickening or viscosity increase. Powdered flavors use carriers that include starch, maltodextrin, sugar, and gums. Flavors using carriers (solvents) are generally used at a higher application level. The source of the carrier should always be considered when making certain label claims, such as gluten free or sugar free.

6.2.5 Storage of Flavoring Materials

As already pointed out earlier, flavoring materials are susceptible to air and light. To control the exposure to light, flavoring materials must be stored in the dark. Light-proof containers or amber glass containers will also protect these materials from light exposure. The exposure to air is more difficult to control. The addition of antioxidants is helpful; however, as soon as a container is opened, exposure to air takes place, and in partially-filled containers the flavoring material is exposed to air during the entire storage time. Efforts should be made to minimize the storage of partially-filled containers. Nitrogen flushing of the headspace of the containers will further reduce the exposure to air. Unfortunately, only too often, flavoring materials are stored in cabinets undated, or in partially-filled containers, and left for months. In most cases the materials will have oxidized, polymerized, or partially evaporated. No flavor will keep indefinitely; however, some, like vanillin, will keep for a very long time. Because of these quality changes in flavoring materials a suitable storage system should be maintained. Most flavors will keep for 6 months to a year. Some encapsulated flavors will keep for up to a year, possibly more depending on the type of encapsulation.

These considerations of flavor shelf life must also be considered in the final candy product. In hard candy or caramel, the flavor once distributed is protected from the air. In aerated products, such as marshmallows, or powders where air is present, the flavor is susceptible to oxidation, and will rapidly degrade. Here an encapsulated flavor is useful.

6.3 Acids in Candies

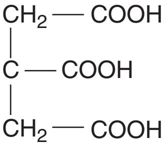
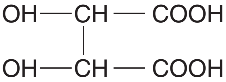
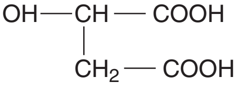
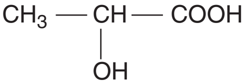
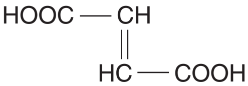
Organic acids find a number of applications in candies and perform different functions. In fruit flavored candies, such as hard candy, they add to the flavor effect. Acids also freshen the palate and prevent dulling of nonacid flavors. They are also used to control the pH in a product. This is of great significance in the setting of pectin jellies (see Section 5.3). Acids also have a preservative effect, partially attributable to the pH. Acetic acid and sorbic acid have a considerable preservative effect.

The flavor profile of most products can be significantly improved by the use of a mixture of acidulants. Mixed acidulants create a more natural flavor profile, since fruits contain mixtures of organic acids. Table 6.8 lists some common fruits, their predominant acid, and their secondary acid(s). Fruits typically contain 0.5–2.0% total acid. Table 6.9 lists the commonly used acids, their empirical formula, their structural formula, and their molecular weight. They are briefly discussed in the following sections.

Table 6.8 Acids naturally present in some common fruits

Fruit	Predominate acid	Secondary acid(s)
Apple	Malic acid	Tartaric and fumaric acids
Apricot	Malic acid	Citric and tartaric acids
Cherry	Malic acid	Tartaric acid
Grape	Malic acid	Tartaric acid
Grapefruit	Citric acid	Malic acid
Lime, lemon	Citric acid	Malic acid
Orange	Citric acid	Malic acid
Peach	Malic acid	Citric acid
Pear	Malic acid	Citric acid
Pineapple	Citric acid	Malic acid
Raspberry	Citric acid	Malic and tartaric acids
Strawberry	Citric acid	Malic and tartaric acids
Watermelon	Malic acid	Fumaric acid

Table 6.9 Commonly used acids, their empirical formula, structural formula and molecular weight (MW)

Acid	Empirical formula	Structural formula	MW
Citric acid	$C_6H_8O_7$	 $\begin{array}{l} CH_2-COOH \\ \vert \\ C-COOH \\ \vert \\ CH_2-COOH \end{array}$	192
Tartaric acid	$C_4H_6O_6$	 $\begin{array}{l} OH-CH-COOH \\ \quad\quad\;\; \vert \\ OH-CH-COOH \end{array}$	150
Malic acid	$C_4H_5O_5$	 $\begin{array}{l} OH-CH-COOH \\ \quad\quad\;\; \vert \\ \quad\quad\; CH_2-COOH \end{array}$	134
Lactic acid	$C_3H_6O_3$	 $\begin{array}{l} CH_3-CH-COOH \\ \quad\quad\;\;\; \vert \\ \quad\quad\;\; OH \end{array}$	90
Fumaric acid	$C_4H_4O_4$	 $\begin{array}{l} HOOC-CH \\ \quad\quad\quad\; \Vert \\ \quad\quad\;\; HC-COOH \end{array}$	116
Acetic acid	$C_2H_4O_2$	CH_3-COOH	60
Propionic acid	$C_3H_6O_2$	CH_3-CH_2-COOH	74
Sorbic acid	$C_6H_8O_2$	$CH_3-CH=CH-CH=CH-COOH$	112

6.3.1 Acids Used as Acidulants

A wide range of organic acids is available to the confectioner (Woo 1998). The choice of which acid, or acids, to use, however, depends on numerous factors. These include the intended flavor profile, what sort of sour impact is desired (note the rise of super sour confections), and, of course, cost considerations.

6.3.1.1 Citric Acid

Citric acid occurs naturally in all citrus fruits. It was first isolated from lemon juice, and lemon juice was the first source of commercial citric acid. Today it is produced by fermentation of sugar syrups or molasses by certain molds. Citric acid is produced in two forms, anhydrous and monohydrate, with molecular weights of 192 and 210, respectively. The acid is hygroscopic, colorless and odorless, and readily soluble in water (62% at 20 °C). In candies, citric acid is mostly used as a 50% solution, although it may also be used in the powdered form. If the powdered form is used, the melting points of the two forms must be considered. The melting point of anhydrous citric acid is 153 °C (307 °F) while citric acid monohydrate, which does not have a sharp melting point, melts at about 130 °C (266 °F). If used in hard candy, at the point the candy is cooled, the monohydrate acid will have melted while the anhydrous acid has not. At that stage, the monohydrate acid will also add a small amount of moisture to the candy. If the anhydrous acid is used, it must be used as a very fine powder to prevent poor dispersion, which may cause sharp-flavored concentrations in parts of the candy.

6.3.1.2 Tartaric Acid

Most consumers are under the impression that tartaric acid is the prevailing acid in grapes. This however is not true - the predominant acid in grapes is malic acid (Table 6.8), although tartaric acid is still an important component of grapes. Tartaric acid is produced from natural products. The acid is found in many fruits, but grape juice is the major source. It is recovered from the press cake during juice production, or potassium hydrogen tartrate (cream of tartar), which separates in the dregs during wine fermentation.

Pure tartaric acid is anhydrous, but hygroscopic. It melts at 168–170 °C (334–338 °F), is colorless, odorless, and has a very tart taste. It is readily soluble in water (60% at 20 °C). It is also soluble in ethyl alcohol. In the past, tartaric acid was widely used a great deal in candies, but it has been replaced for the most part by citric acid. Tartaric acid has a sharper taste compared to citric acid, which can cause undesirable flavors.

6.3.1.3 Malic Acid

Malic acid, sometimes called pomulus acid, is a widely distributed acid in fruits (Table 6.8). Although it is the principal acid in apples, much, if not all, of the commercially available ingredient is produced synthetically by hydration of maleic anhydride. The resulting product, used commercially, is a racemic mixture of equal parts of the two optically active compounds, D and L forms, whereas only the L form is found in nature.

Malic acid is an anhydrous, colorless crystal with a melting point of 128–129 °C (262–264 °F). It has found application in hard candy, and is often used in conjunction with lactic acid. These acids may be buffered, usually with sodium lactate, to give a high enough pH to reduce the inversion of sucrose, but retain the acid taste.

6.3.1.4 Lactic Acid

Lactic acid is widely distributed in nature. It was discovered in soured unpasteurized milk. Commercially, it is prepared by the fermentation of sugars such as sucrose, lactose, dextrose, and other fermentable material such as starch, and whey. The fermentation is induced by lactic acid bacteria. The specific organism used depends on the raw material to be fermented. Purification involves the formation of calcium lactate and decomposition of the salt with sulphuric acid.

Lactic acid is a thick hygroscopic liquid that does not crystallize, but is miscible with water. It is a pleasant-flavored acidulant and can be buffered with sodium lactate, which is also liquid. The buffered lactic acid finds application in continuous hard candy production, where it can be directly injected into the boiled liquid as it leaves the cooker (see Chapter 8). The buffered lactic acid gives a pH high enough to minimize sucrose inversion.

Another useful property of lactic acid is the solubility of calcium lactate. Many products, even the water supply, contain enough calcium that will be precipitated as a haze (calcium citrate) if citric acid is used as the acidulant. This is overcome by the use of lactic acid, and is useful in the manufacture of fruit gums to retain the bright, clear appearance.

Lactic acid also has a slight preservative effect. It has been used to inhibit fermentation in fondants, and 0.2–0.4% is effective in syrups of concentration down to 70%.

6.3.1.5 Fumaric Acid

Fumaric acid is a nonhygroscopic crystalline substance. It is only slightly soluble in water (0.5% at 20 °C). Because it is not hygroscopic, it finds application where noncaking properties are required, as in powders. The moisture absorption of citric vs. fumaric acid is illustrated in Figure 6.1. It is also used in gelatin candies to enhance gel strength and to improve the whipping qualities in egg albumen.

6.3.1.6 Acetic and Sorbic Acids

Although not used for the traditional acid effect in candies, these acids are important for their antimicrobial properties. Acetic acid has only a mild preservative effect. It is the final product of several aerobic fermentations. The pure acid is a strong corrosive acid with a pungent odor. It has been used as a preservative in marzipan, pastes, and some fondants. In fondant of a syrup phase concentration between 70% and 75%, the addition of 0.5–0.7% of acetic acid can prevent fermentation by yeasts. However, because of its vinegar taste, addition of above 0.10% causes flavor detection by most flavor panelists.

Sorbic acid is a much preferred antimicrobial agent. It is found naturally in the unripe sorp apple (*Sorbus aucuparia*/mountain ash). In pure form, it is a white crystalline powder with a slightly acid, but pleasant taste. It melts at 130–134 °C (266–273 °F). Its solubility at 20 °C is

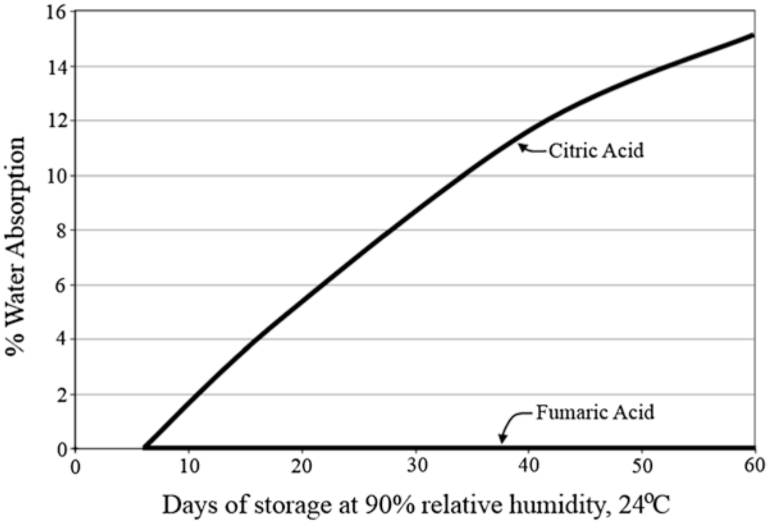


Figure 6.1 Water absorption of citric vs. fumaric acid

0.16% in water, 14.0% in 95% ethyl alcohol and 0.5% in glycerol. The effectiveness of sorbic acid is greatest at pH values below 6.0. Under these conditions it inhibits molds and yeast, and some bacteria.

Most candies do not require a preservative, but if high water activity ingredients, like fruit puree and soft fillings, are used, sorbic acid may be useful. Permitted usage level varies from country to country, but in general a level between 0.10% and 0.20% is effective in fondant, marzipan, and nut pastes.

6.3.2 Sourness

It is generally recognized that the level of sourness is determined by the specific acid used, the hydrogen ion concentration, pH, and the concentration of the acid. The taste sensation of organic acids differ (Solms 1971). The taste sensations of citric acid, malic acid, lactic acid, and tartaric acid have been described as fresh, green, sour, and harsh, respectively. In addition to the above-mentioned factors, sourness is also influenced by the presence of buffers and other compounds, especially sugars. Figure 6.2 shows the change of relative sourness of acids as a function of pH. At pH 3.0, malic acid is significantly more sour than citric acid, although they have the same level of sourness at pH 4.7. Similarly, fumaric acid is more sour than citric acid at pH 3.0, but the acids provide an equal sour sensation at pH 4.0. In every case, sourness increases with decreasing pH. Since acids release hydrogen ions in solution resulting in a decrease in pH, if an acid is added to a product, sourness will increase, assuming no other changes take place. Even though two acids may provide the same level of sourness at a certain pH value (citric and malic acid at pH 4.7), because of their specific flavor, products in which they are used would not taste the same.

In addition to the pH, sourness is impacted by the amount of un-dissociated acid present in the system. Undissociated acids are more sour than dissociated acids. To achieve more sourness at a specific pH, an acidulant should be chosen that leads to more undissociated acid. Because of these effects, sourness is influenced by the dissociation constant (pKa) of an acid. The pKa value is the pH value where the levels of undissociated and dissociated molecules are equal (half dissociated and half undissociated).

When food acids are dissolved in water, they dissociate to yield hydrogen ions. The number of hydrogen ions released during dissociation varies depending on the acid used. Monoprotic acids, such as acetic and lactic acids, release one hydrogen ion. Diprotic acids, such as fumaric, malic and tartaric acids, release two hydrogen ions. Triprotic acids, such as citric acid, release three hydrogen ions. As the pH increases all acids

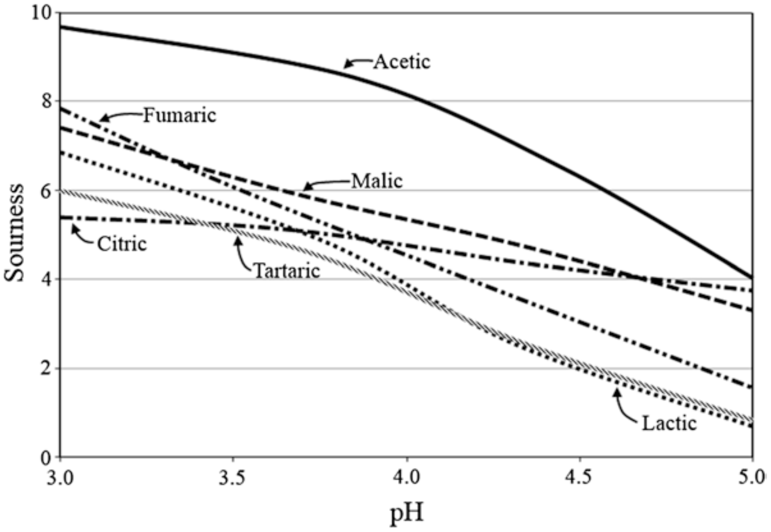


Figure 6.2 Sourness of acids at 0.2% w/v vs. pH (from Woo and Symanski 2001, with permission)

become more dissociated. The dissociation of monoprotic, diprotic and triprotic is illustrated below:

$$\text{Monotropic acid} \xrightarrow[\text{pH}]{} H^{+} + HA + A^{-}$$

$$\text{Diprotic acid} \xrightarrow[\text{pH}]{} 2\,H^{+} + H_2A + HA^{-} + A^{--}$$

$$\text{Triprotic acid} \longrightarrow 3\,H^{+} + H_3A + H_2A^{-} + HA^{=} + A$$

The dissociation of acetic acid (monotropic) is illustrated in Figure 6.3. At pH 4.76, the pKa of acetic acid, 50% of acetic acid and 50% of acetate ion are present. At pH 3.0, almost all of the acetic acid present is undissociated. The undissociated acetic acid is much more sour than the dissociated acetate ion. At pH 6.0, the reverse is true, where almost all the acetic acid is dissociated into the acetate ion. The acetate ion is not very sour, but chelates metal ions. Sourness and chelation are inversely related.

The dissociation of acetic acid compared to lactic acid is illustrated in Figure 6.4. Since the pKa value of acetic acid (4.76) is higher than lactic acid (3.86), at any pH value there will be more undissociated acetic acid present than undissociated lactic acid. Acetic acid is more sour because of the high pKa, which results in a high value of undissociated acetic acid at a pH of many candies. However, the intense flavor of acetic acid limits its application. To achieve a more intense sour flavor using lactic acid, the candy should have a pH below 4.0.

The dissociation of malic acid (diprotic acid) is more complex, as illustrated in Figure 6.5. Malic acid, a diprotic acid, has two pKa values. The first pKa_1 is 3.40; at this value, there are equal quantities (50%) of undissociated malic acid (H_2A) and dissociated acid malate ion (HA^-). The second pKa_2 is 5.11, where there are equal quantities (50%) of acid malate ion (HA^-) and completely dissociated malate ion ($A^=$).

As with monoprotic acid, malic acid becomes less sour as it dissociates even though the acid malate is still quite sour. With greater dissociation the ability to chelate metal increases.

6.3.3 Buffer Salts

The definition of a buffer is "any substance in solution that tends to stabilize the hydrogen ion concentration by neutralizing any added acid or alkali". For example, solutions of sodium chloride or ammonium acetate each have a pH of 7.0. If 1 ml of a 0.1 N hydrochloric acid is added to one liter, the pH of the sodium chloride solution will decrease to 4.0, while the pH of the ammonium

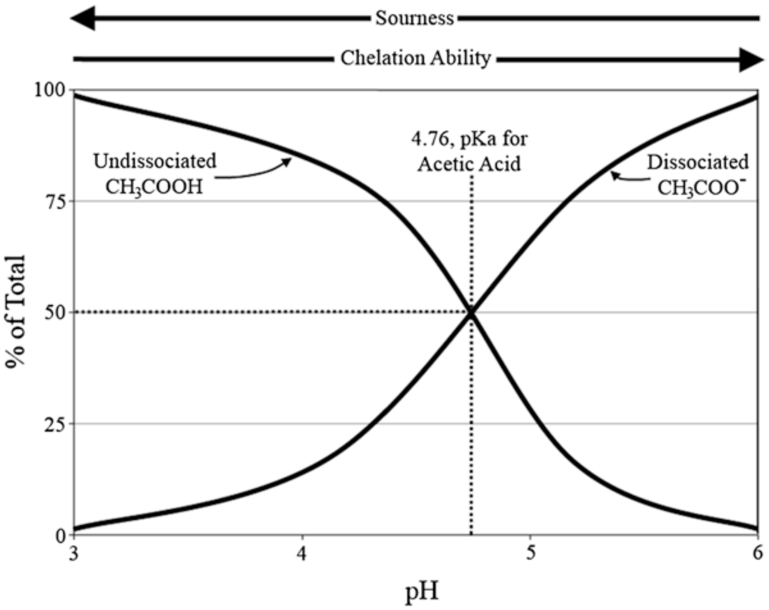


Figure 6.3 Dissociation of acetic acid vs. pH (from Woo and Symanski 2001, with permission)

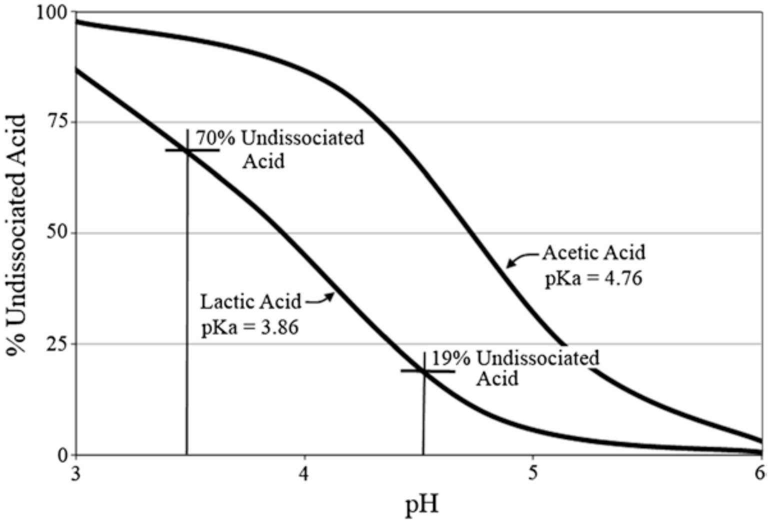


Figure 6.4 Dissociation of acetic and lactic acid vs. pH (from Woo and Symanski 2001, with permission)

acetate solution remains virtually unchanged. In this case, ammonium acetate acts as a buffer.

In the manufacturing of confections, it is often required to control the pH, and this is achieved by the use of buffer salts. Typical buffer salts used include sodium, potassium, and ammonium acetate, citrate, and lactates. Buffers in confections are used to prevent the inversion of sucrose, to prevent gelatin hydrolysis, to control gelling of pectin, and to minimize flavor variation.

Buffer capacity is the ability of a buffer to resist change in pH. Buffer capacity is a function of the molarity and increases as the buffer salt/acid solution increases. It is expressed in terms of the molarity of sodium hydroxide required to increase the pH by 1.0 pH unit. The buffering capacity is the greatest when the pH is closest to the pKa value of the acid. Figure 6.6 illustrates the effect of pH and molarity on the buffer capacity. Acids like acetic and lactic acid have higher molarities and therefore, have a greater peak

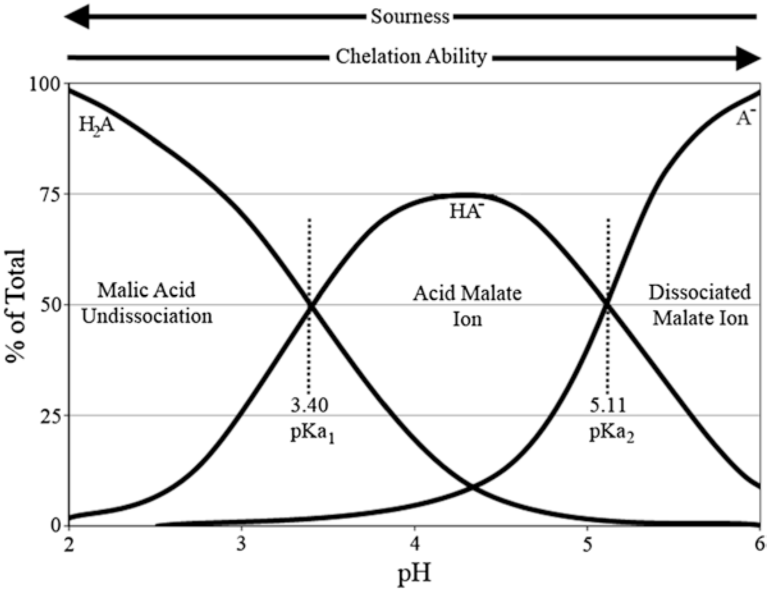


Figure 6.5 Dissociation of malic acid vs. pH (from Woo and Symanski 2001, with permission)

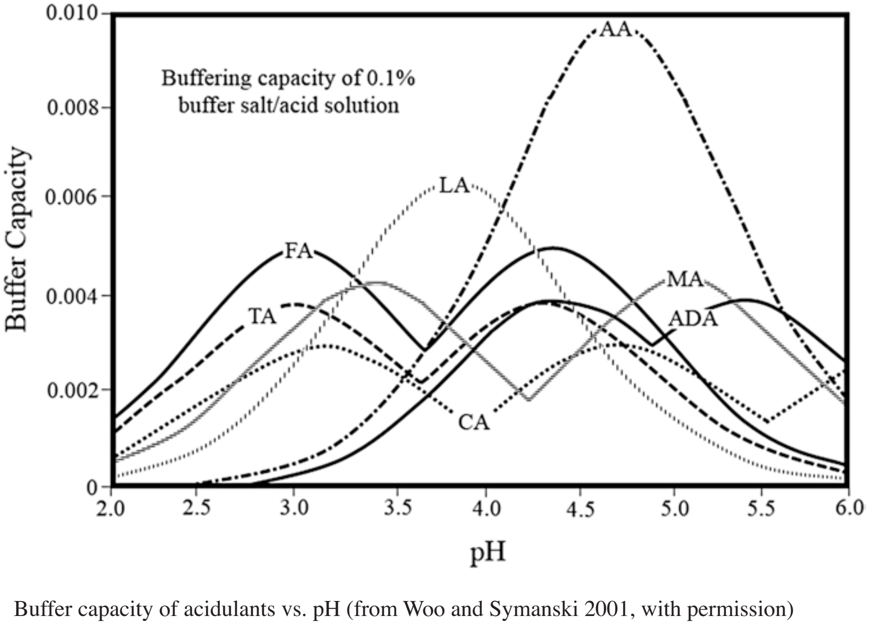


Figure 6.6 Buffer capacity of acidulants vs. pH (from Woo and Symanski 2001, with permission)

buffering capacity compared to other acids. These acids also have a narrow range of application compared to other acidulants.

In pectin confections, the final pH is 3.2–3.5; therefore, the acids of choice as a buffer would be lactic (pKa 3.86) or malic acid (pKa_1 3.4). Gelatin containing confections have a final pH of 4.5–5.0; here, acetic acid (pKa 4.76) or malic acid (pKa_2 5.11) would be the acid of choice.

6.4 Antioxidants

All plant and animal products contain a variety of antioxidants to protect against lipid oxidation. The most important natural antioxidants are the tocopherols, lecithins and ascorbic acid, although many other phenolic compounds possess antioxidant properties, such as anthocyanins and flavonoids. The latter are found in many fruits and vegetables.

6.4.1 Mechanism of Oxidative Rancidity

The first step in the development of rancidity in fats or oils is a process of autooxidation, when air comes in contact with a lipid material. This process can be accelerated by external factors, such as light, heat, or traces of metals, specifically iron and copper. The result is the formation of peroxide radicals in the fat or oil and these enable the fat itself to react with oxygen. Thus, a continuous reaction is set up. See Section 4.2.3 for more detail.

The deterioration of a fat can be measured by determining the peroxide value. Rancidity is detectable if the peroxide value reaches 20 in animal fats and 50 in vegetable oils. The time needed for a fat to reach the peroxide value is called the induction period. An accelerated test is often applied to measure the induction period. In the test, air is bubbled through a quantity of liquid fat at 98 °C (208 °F). Peroxide values are taken at intervals, plotted on a graph and the time to reach a peroxide value of 20 is estimated.

6.4.2 Action of Antioxidants

Antioxidants are used to increase the oxidative stability by control of free radicals, oxidation intermediates, and pro-oxidants. Many antioxidants slow down oxidation by scavenging free radicals. Free radical scavengers inhibit lipid oxidation by reacting faster with the free radical than the unsaturated fatty acid. The tocopherols are an example of free radical scavengers. Oxidation intermediates are controlled by compounds found in foods that impact lipid oxidation by interacting with pro-oxidant metals or oxygen to form reactive groups. Hydroperoxides are an example of such compounds. The rate at which oxidation of lipids proceeds depends on the concentration of pro-oxidants. Control of these, therefore, is very important to extend the shelf life of fats and oils.

As stated earlier, iron and copper are examples of pro-oxidants. They accelerate lipid oxidation by promoting hydroperoxide decomposition. Certain substances are able to reduce the catalytic effect of metals. These are known as sequestering agents, and include citric acid, phosphoric acid, and EDTA (ethylene diamine tetra acetic acid). Sequestering agents have a synergistic effect with the primary antioxidant; therefore, the best protection is given by a mixture of antioxidants and a sequestering agent.

Most fats and oils contain natural antioxidants (to varying extent), the most important of which are tocopherols. Some fats have glyceride structures that render them more prone to rancidity. Vegetable fats usually contain greater amounts of natural antioxidants than animal fats and therefore added antioxidants have a greater protective effect in animal fats. Cocoa butter is a good example. It contains sufficient natural antioxidants and stable glyceride structures to keep it free from rancidity for very long periods. In contrast, fish oils, which contain numerous polyunsaturated fats, are very susceptible to oxidation and become rancid quickly. Here, added antioxidants can provide additional protection. Natural antioxidants are only partially effective, and under certain circumstances are not heat stable for example, during fat deodorizing or deep frying.

Antioxidants have no protective effect against hydrolytic rancidity. Hydrolytic rancidity is enzyme catalyzed, where the fat is hydrolyzed into glycerol and fatty acids. This type of rancidity is recognized by the presence of soapy flavors and higher free fatty acid (FFA) values, due to the hydrolysis of the fat. Oxidative rancidity gives tallowy or fishy flavors and may be detected analytically by determining the FFA content or peroxide value. Typical good quality vegetable oils have FFA values lower than 0.05% (as oleic acid) and 1.0 mEq/kg peroxide.

Primary antioxidants terminate free radical chains and function as electron donors. They include the phenolic antioxidants, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butyl hydroquinone (TBHQ), alkylgalate, propylgalate (PG), and natural and synthetic tocopherols. Their chemical structures are illustrated in Table 6.10. The permitted use of these antioxidants varies between states and countries and should be investigated before incorporating into finished products.

Oxygen scavengers also help to delay oxidation by removing oxygen in a closed system. The most widely used compound is ascorbic acid, and related substances, ascorbyl palmitate and erythorbic acid (the D-isomer of ascorbic acid).

Pro-oxidants can be removed by chelating agent or sequestrants. As mentioned above, two widely used sequestrants are citric acid and EDTA.

Antioxidants are added to products by solubilizing them in some of the fat or another solvent and adding to the bulk. They can also be sprayed on the products. Sometimes antioxidants are embodied in the wrapping materials used for fatty foods where fat may spread as a thin layer over the wrapper surface. Thin films are very prone to oxidative rancidity. The amount of antioxidant embedded must be carefully controlled, because the transfer of antioxidant to the food may not exceed the permitted limit. In the United States, the maximum allowed level is 0.02% based on the fat content of the food.

6.5 Glazes and Waxes

Glazes and waxes are used in the manufacturing of confections, mainly to enhance appearance but also as protective coatings on panned candies. In addition to forming a moisture barrier and extending the shelf, they also help to prevent stickiness.

6.5.1 Glazes or Lacquers

Glazes are applied to candies to retain freshness, heighten appearance and gloss. They provide a moisture barrier to minimize loss of gloss during high humidity conditions, and may help protect heat-sensitive confections at higher than optimal temperature storage conditions. There are two major glazes used in the manufacturing of candies, shellac and zein, with shellac far outweighing zein in terms of application.

6.5.1.1 Shellac

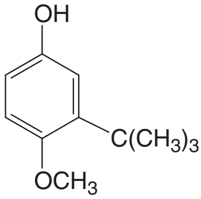
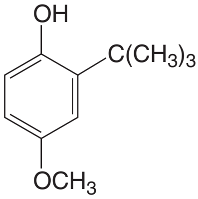
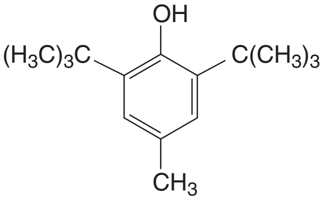
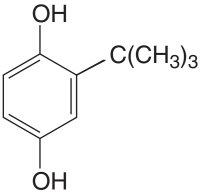
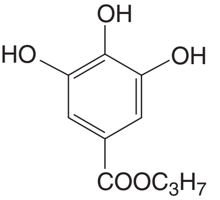
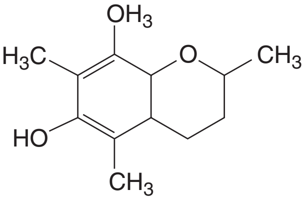
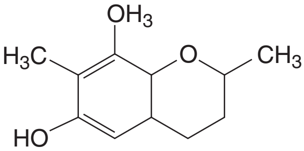
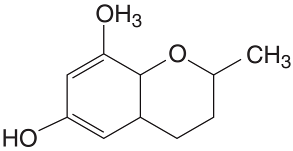
Shellac is used as a glaze particularly for panned candies. The word shellac refers to all forms of purified lac. Lac is the hardened resinous secretion of the tiny scale insect, *Laccifer lacca,* of the family *Coccidae.* It is a parasitic animal that uses certain trees and shrubs as its host, and secretes a resin as a protective shell for its larva. The female secretes most of the resin. The resin is hard, tough, and amorphous, and has good water resistance and produces high sheen finishes. Along with the resin, a small amount of wax is produced. The wax prevents the pores of the insect from becoming blocked by the resin.

After the life cycle of the insect is completed, the encrusted twigs are collected by cutting off the branches and then reducing them into small pieces. The lac at this stage is known as "sticklac". The sticklac is scraped to remove the lac, or crushed to separate the lac resin from the sticks. The crushed lac contains a mixture of resin, insect remains, dye, twigs, and other impurities. This mixture is now passed through a coarse screen to remove larger sized twigs. The screened material is washed with water to remove the water-soluble dye and float off small pieces of twigs and insect bodies. After several washings, the ground lac is dried. This product after drying and grinding is known as "seedlac".

Two physical processes are used to manufacture shellac, heat or solvent process. In the heat process, shellac is made by melting the seedlac with steam, and then forcing the molten lac by means of hydraulic pressure through a fine-wired screen. The filtered molten shellac is transferred to a steam heated kettle, from which it is dropped onto rollers, squeezed out, and removed in the form of a thin sheet. The shellac produced by this process contains wax.

The solvent process produces three types of shellac: dewaxed, dewaxed decolorized, and

Table 6.10 Chemical structures of antioxidants

Antioxidant[a]	Chemical structure(s)
BHA	 3-tertiary-butyl-4-hydroxy-anisole  2-tertiary-butyl-4-hydroxy-anisole
BHT	 2,6-ditertiary-buty1-4-methylphenol
TBHQ	 tertiary-butylhydroquinone
Propylgallate	 propanol ester of: 3,4,5-trihydroxybenzoic acid
Tocopherol	 Alpha-tocopherol  Gamma-tocopherol  Delta-tocopherol

[a] *BHT* butylated hydroxytoluene, *TBHQ* tertiary butylhydroquinone, *BHA* butylated hydroxyanisole

wax-containing. For wax-containing shellac, the seedlac and solvent, ethyl alcohol, are mixed in a dissolving tank at a ratio of 1: 4 by weight. The mixture is refluxed for 1–2 h and then filtered to remove undissolved lac and other alcohol insolubles. The filtrate is then concentrated in a series of evaporators into a viscous mass, which is then dropped onto rollers to produce thin sheets and removed in flake form.

Dewaxed shellacs are made by dissolving the seedlac in either high proof alcohol or weaker proof alcohol at elevated temperature. The solutions are then concentrated by evaporators and the concentrate is dropped onto rollers, squeezed and removed in flake form.

Dewaxed, decolorized shellacs are produced by the same method as dewaxed shellac, except that after dewaxing the solutions are treated with activated charcoal to remove the dark colored materials in the shellac. By varying the contact time and the amount of activated carbon, shellacs, varying in color from light yellow to a dark orange, can be produced.

Shellac may also be bleached, in either wax-containing or wax-free forms. Here, the seedlacs are dissolved in aqueous alkali solution, generally sodium carbonate, at high temperature. The solution is then centrifuged to remove insoluble lac and other insoluble impurities. For wax-containing bleached shellac, the centrifuged solution is then bleached with a dilute solution of hypochlorite to the desired color. The shellac is then precipitated from the solution with dilute sulfuric acid, after which it is filtered, washed with water and dried. Dewaxed shellac is dewaxed either before or after bleaching. The dewaxed solution is precipitated, washed, and dried by the same method as wax-containing shellacs.

Bleached shellac is generally used for glazing of panned products. Regular confectionery glaze is prepared from food-grade bleached shellac and contains 5% wax. The solution has an opaque appearance, but produces a transparent film. The wax acts as a plasticizer and thus, provides for a more flexible film.

Wax-free confectionery glaze is made from wax-free bleached shellac. It is less viscous compared to regular confectionery glaze, and therefore can be used at higher concentrations. The dried film is very clear. It is often used as a finishing coat over waxed coatings. In either glaze, the concentration of the bleached shellac may range between 22% and 45%. Lower concentration levels are used when low viscosity is needed to provide adequate coverage (for example, in non-pareils). However, the Code of Federal Regulations (CFR) specifies a minimum level of shellac that must be added to alcohol to qualify as denatured (and thereby avoid liquor taxes). According to the CFR, 300 lb of shellac must be added to 100 gallons of alcohol. This concentration is called a 3-lb cut (a pound cut is defined as pounds of shellac added per gallon of alcohol) and equates to about a 31% concentration of shellac in the alcohol. When lower concentrations of shellac are needed, another denaturant such as ethyl acetate must be used to ensure the alcohol is denatured. This may preclude its use in organic confections.

In addition to the two above-mentioned glazes, orange confectionery glaze may be used under certain conditions. For one, it can be used on dark colored items where its color is not a concern, but it is also used for organic products where bleached shellac may be disqualified for use. Orange confectionery glaze is made from orange colored flake shellac. The glazes are dissolved in alcohol and applied at 0.1–0.3% usage level by weight. It is recommended, when alcohol containing glazes are used, that the product be first sealed with aqueous polishing agent to block the absorption of solvent and to eliminate residual solvent odor in packages product.

6.5.1.2 Zein

Zein glaze is sometimes used when shellac is unacceptable; for example, in vegan applications. Zein glaze refers to an alcohol-soluble protein derived from the corn endosperm. It produces a flexible film that is free of color, odor, and flavor. Besides being soluble in alcohol, it is soluble in isopropyl alcohol in range of 5–20% of the total weight of the solution. Plasticizers such as glycerol and propylene glycol are used in zein solutions. Zein and shellac suppliers have chemically modified these products to make them water soluble.

6.5.2 Waxes

Several waxes have found application as polishes in the confectionery industry. The primary waxes used include beeswax and carnauba wax, although candellila wax has been used in the past. The usage level ranges between 0.05% and 0.1% by weight. They can be used in powdered form or dissolved in food-grade solvents such as alcohol. In some cases, mineral or vegetable oils are added to lubricate and smooth the candy surface. Powdered waxes can cause white spotting on dark and colored candy surfaces, because of wax particles that become embedded in the crevices of the candy surfaces.

6.5.2.1 Beeswax

Beeswax is secreted by honey bees for the production of their combs. After the honey has been removed by centrifugation from the combs, crude wax is obtained by melting the wax in hot water and straining it through cloth or fine screens. The wax can also be bleached with a solution of hydrogen peroxide. The melting point of beeswax is 61–70 °C (142–156 °F).

6.5.2.2 Carnauba Wax

Carnauba wax is a plant wax obtained from the leaves of the plant *Copernica cerifera*. It has a higher melting point than beeswax [78–85 °C (172–185 °F)]. It is a hard wax that imparts gloss to panned products. Used alone it can cause a gray haze on the candy surface. This can be overcome by using a mixture of beeswax and carnauba wax.

6.5.2.3 Candelilla Wax

Candelilla wax is a plant wax, derived from the leaves of the candelilla shrub. The shrub is native to northern Mexico and southwest United States. The wax is obtained by boiling the leaves in dilute sulfuric acid and skimming from the surface. It is insoluble in water, but soluble in organic solvents. The wax's melting point is 67–79 °C (153–174 °F). It has a yellowish-brown color.

6.6 Fruit and Fruit Products

Fruit products, jams, fruit preserves and dried fruits find wide application as ingredients in the manufacturing of confections. They have been used as ingredients in fondant, jellies, gums and chocolates. Because the natural fruit flavors are delicate and not strong enough, particular in conjunction with chocolate, they have to be reinforced with added flavors. Citrus fruits, with their natural essential oils, provide a strong enough flavor in most products.

6.6.1 Composition of Fruits

Table 6.11 gives average composition values for some selected fruits. There is great variation in composition not only from fruit to fruit, but also between cultivars, growing season, horticultural practices and production areas.

6.6.2 Jams, Preserves and Purèes

In the United States, jams and preserves are defined by a Standard of Identity, which states that the finished product must have a soluble-solids content not less than 65%, as determined by refractometer. Jams sold for general consumption have a soluble solid content between 65% and 70%, which is too low if the jam is to be used as a filling for chocolate shells or fondants. At 70% soluble solids or below, if not under refrigeration, microbiological spoilage can occur from osmophilic yeasts and molds.

For confectionery fillings, the soluble solid content should be between 75% and 78% to prevent spoilage. However, higher soluble solid content can lead to sugar crystallization. Jam suppliers, therefore, produce for the confectionery industry a "confectionery jam". Also, in certain applications,

Table 6.11 Composition of some selected fruits

	Moisture	Protein	Fat	Carbohydrate	Fiber	Calcium	Iron	Vitamin A	Vitamin C
Fruit	%	g/100 g	g/100 g	g/100 g	g/100 g	mg/100 g	mg/100 g	IU/100 g	mg/100 g
Apples, raw	84.8	0.2	0.1	14.1	1.0	3.0	0.10	90	7.0
Dried	32.9	0.9	0.3	64.8	2.8	15.0	1.7	–	3.0
Apricots, raw	85.3	1.0	0.2	12.8	0.6	8.0	0.5	2,700	10.0
Dried	31.5	3.9	0.5	60.8	2.9	51.0	4.8	7,147	3.0
Cherries, sour	83.1	1.2	0.3	14.3	0.2	0.6	0.4	1,000	10.0
Black currant, raw	84.2	1.7	0.1	13.1	2.4	60.0	1.1	2,300	200.0
Dates, dried	23.8	1.9	0.5	72.2	2.3	32.0	1.04	50	–
Figs, raw	77.5	1.2	0.3	20.3	1.2	36.0	0.4	80	2.0
Dried	25.8	3.1	1.5	67.3	4.7	0.5	2.06	133	–
Grapefruit, white	87.7	0.5	0.1	11.3	0.2	15.0	0.3	10	30.0
Lemons, w/o peel	87.4	1.2	0.3	10.7	5.1	61.0	0.7	30	77.0
Lime, w/o peel	89.3	0.8	0.2	9.5	0.5	33.0	0.6	200	24.0
Prunes	32.4	2.6	0.5	62.7	2.5	51.0	2.47	1,994	3.3
Oranges, w/o peel	86.0	0.9	0.2	12.2	0.5	41.0	0.4	200	50.0
Raisins, seedless	17.0	3.0	0.2	77.2	0.8	86.0	2.7	20	0.9
Raspberries, red, raw	84.2	1.2	0.5	13.5	3.0	22.0	0.9	130	25.0
Strawberries, raw	89.9	0.7	0.5	8.4	1.0	21.0	1.0	60	59.0

Source: Ensminger et al. (1994)

such as filled chocolate shells, a high fruit content is desirable to obtain maximum flavor.

To make this type of jam, a base syrup prepared from sucrose, invert sugar, and sometimes liquid glucose is boiled to a concentration of 85–87% and fruit or fruit purèe is mixed in rapidly. This process results in a mixture of sugars and fruit with a soluble solid content of 75–78%. In some instances, a short boil may be required to reach the desired soluble solid content. These specialty jams may be used as prepared or may be mixed with a pectin syrup to obtain a partial set after depositing.

Some confectionery manufacturers may choose to make their own jam fillings from canned or frozen fruit purèes. The advantage here is that fillings with higher fruit content may be obtained. In this case, the purèes are first vacuum concentrated and, based on the soluble solid content, the required amount of sugars, sucrose/invert sugar/glucose, is added at the end of the vacuum cook. The vacuum boiling is continued until the desired soluble solid content (75–78%) is reached.

6.6.3 Candied and Preserved Fruits

Candied fruit pieces are used as centers and in bars and in some nougats. Cherries and pineapple are the most popular fruits to be candied, but other fruits such as apricots, apples, pear, and prunes can be candied. The peels of citrus fruits, particularly from oranges and lemons, make excellent candied products, and because of the natural essential oils in the peel, they retain their flavor for extended shelf life. Candied fruits are either prepared by a batch or continuous process.

Fruits that have a rigid tissue structure are candied either whole or in halves. Cranberries, for example, must be halved or the skin perforated, in order for sugars to penetrate the fruit. Soft fruits, strawberries and raspberries, are difficult to preserve. Some success has been possible with a continuous process.

For fruits with strong cell structure, such as cherries and pineapple, preservation must take place in syrups of gradually increasing concentration. This is true for the batch as well as the continuous process. If fruits are immersed in hot 75% concentrated syrup, the osmotic pressure will cause water to pass outward through the cell wall more quickly than the syrup passes inward. The difference of the rates of passage of water and syrup causes the collapse of cell structure and the fruit will become tough and shriveled.

6.6.3.1 Batch Process

The fruit is washed, stemmed, and de-stoned, or whatever unit operation is applicable, then immersed in boiling water (blanched) for a short period to soften it, and to remove tissue gas, but it must remain whole. After draining, the fruit is immersed in a 30–40% sugar syrup consisting of sucrose and glucose, or sucrose, glucose and invert sugar. The invert sugar is added to decrease the viscosity of the final syrup at 75–78% soluble solid concentration. Immersion in this syrup continues for 16–24 h, and after the fruit is drained off, the concentration is increased to 60–65% soluble solids, and the fruit is returned for an additional 24 h. After the second immersion, the syrup is slightly warmed to reduce the viscosity and promote drainage. The concentration and immersion are repeated at least twice more until the soluble solids content of the fruit reaches 75–78%.

6.6.3.2 Continuous Process

The unit operations prior to immersion in the syrup are similar in the continuous process to the batch process. After the fruit is blanched, it is drained and placed into a series of baskets held in a cage, which can be lowered into the processing vat containing the syrup. The syrup is a mixture of sucrose and corn syrup to give a concentration of 30–40%. After the fruit is immersed, the vat is closed, and by the use of a circulatory pump, the syrup is forced between the fruit and slowly concentrated under vacuum.

With this system, the static conditions of the batch system are eliminated and the fruit is impregnated by osmosis without shrinkage. The cage of processed fruit is lifted from the vat and most of the syrup is drained off. Final draining is done by placing the trays in a hot room where complete draining and slight surface drying take place.

6.6.3.3 Crystallized and Glacé Fruit

Crystallized fruits are prepared from candied fruits. They are then immersed in a high concentration syrup to form a sugar film. The syrup is prepared by dissolving sucrose in water to 70% concentration and then boiling to 80% concentration. The syrup is allowed to cool until the first sign of crystallization occurs when the candied fruit is immersed. Once crystallized, the fruit is drained on wire racks, and then dried in a warm room. Glacé fruits are similar to crystallized fruits except the syrup is formulated so that it does not crystallize. The enrobing syrup remains soft, flexible, and sticky.

6.6.4 Dried Fruits

Dried fruits are prepared by either sun drying, atmospheric drying, vacuum drying, or freeze drying. In any of these processes, it is essential that the moisture content is reduced to give a water activity $<\approx 0.6$, at which point microbial spoilage is avoided. A brief description of the different drying processes is provided here. For more information, the reader is referred to engineering or processing books dealing with the various drying processes (Fellows 2000; Singh and Heldman 2009).

Sun drying is the oldest drying method and is limited to areas of the world where sunny weather can be guaranteed after the fruit has ripened. Dates, figs, and some grapes are dried by this method. However, sun-dried fruits have not always been produced under the best sanitary conditions. The fruits often contained dirt, insect fragments, and other contaminants. Today, to improve the sanitary conditions, the fruit is exposed to sulfur dioxide for several hours before drying. This prevents attack by microorganisms and improves the appearance of the fruit. The fruit is also placed on trays to improve the sanitation during the drying process.

Atmospheric drying is carried out in tray dryers or tunnel dryers. The fruit is spread in thin layers on trays or belts and subjected to an air current at temperatures between 60 and 77 °C (140–170 °F). Prunes, which are made from a special type of plum, are dried in a tray drier; because they are dried whole, the process may take up to 2 days. To preserve the appearance (color), the fruits are exposed to sulfur dioxide.

The advantages of vacuum drying are the use of lower temperatures, shorter drying times, and better retention of nutrients. However, it is more expensive compared to atmospheric drying methods.

Freeze drying is the most expensive drying method, but it results in a superior product. The process involves the sublimation of ice from the fruit, at a temperature below the freezing point under a high vacuum (less than 0.5 mmHg). The process is also referred to as lyophilization. The fruit retains its shape and flavor remains imbedded within the glassy dried fruit matrix. However, because of the porosity, it is subject to oxidation and the dry powder is very hygroscopic.

6.7 Nuts

Nuts are an important food, consumed by most people. They have a pleasant flavor, are not sweet, have a crunchy texture, and are nutritious. In confections, nuts are an important ingredient. They are used as centers in chocolate enrobing, as flavor enhancers (e.g., peanut brittle), and as pastes and small particles.

6.7.1 Composition

Nuts greatly contribute to the nutritional value of confections. They have a high protein content, their fats are unsaturated fats, they have a significant mineral content (ash content), particularly phosphate and potassium, and contain some vitamins (although not a significant source). Data in Table 6.12 give some average composition values for various nuts. Variation in composition occurs between lots, origin, growing conditions, and types.

Table 6.12 Composition of selected nuts

						Minerals (mg/100 g)				Vitamins (IU or mg/100 g)		
Shelled nuts	Moisture (%)	Protein (g/100 g)	Fat (g/100 g)	COH (g/100 g)	Fiber (g/100 g)	Ca	P	K	Fe	A	D	C
Almonds	–	18.6	53.9	19.5	14.3	234	504	773	4.7	0	0	–
Brazil nuts	4.6	14.3	68.2	10.9	3.1	186	693	715	3.4	0	0	10
Cashew nuts	5.2	17.2	45.5	29.3	1.4	38	373	464	3.5	100	–	–
Coconut, dried	3.5	7.2	64.9	23.0	3.9	25	187	588	3.3	0	–	–
Hazelnut	3.3	13.2	66.7	12.8	1.9	–	360	–	2.4	–	0	0
Macadamia nuts	3.0	7.8	75.7	15.5	2.5	48	161	264	2.0	–	–	–
Peanuts	5.4	25.3	49.7	17.6	1.9	59	409	674	2.2	360	–	0
Pecans	3.4	9.4	71.4	14.6	2.3	73	200	603	2.4	130	–	2
Pistachio nuts	5.3	18.9	53.6	19.0	1.9	131	500	972	7.3	230	–	0
Walnuts, black	3.1	20.5	59.6	14.8	1.7	–	570	460	6	300	–	–

Source: Ensminger et al. (1994)

6.7.2 Varieties of Nuts

A large variety of nuts are available to the confectionery manufacturer. They include almonds, Brazil nuts, cashew nuts, coconut, hazelnuts or filberts, macadamia nuts, peanuts, pecans, pistachio nuts and walnuts. A brief discussion of each follows.

6.7.2.1 Almonds

Almonds probably find the greatest acceptance of all nuts by the consumer. Their value as a food has been recognized for many years. About 80% of the almond production comes from California. In Europe, almonds are grown in Spain and Portugal, with minor quantities grown in Afghanistan, Tunisia, Cyprus, and Libya. The tree requires a warm but not tropical climate.

All California almonds are machine harvested. The nuts, after being shaken from the tree after collection, are hulled and shelled. Ideally, almonds are dried naturally rather than mechanically. Mechanical drying may be needed if the kernels are moist, which can be caused by poor weather conditions, and the possibility of mold development exists.

There is a great variety of almonds, but the most prominent variety is the soft-shell variety. It makes up 60% of the California crop. Another famous almond is the Jordan almond, produced in Spain. The kernels vary greatly in size. They are available in raw form, blanched, blanched and sliced, and roasted.

Blanching of almonds involves immersing the kernels in boiling water for a brief period. This loosens the skin, which is removed by squeezing the kernel through rubber-faced rollers. The blanching process is also essential for the destruction of enzymes and certain microorganisms. The wet kernels are immediately dried.

Roasting of almonds improves the flavor and increases the crispness of the kernel. Roasted almonds find numerous applications in chocolates, caramels, nougats and toffees. In caramel and toffees, the raw almonds are often roasted during the manufacturing process. In chocolate panning, almonds are often used as centers. Almond butter is made similar in consistency to peanut butter. It is made by grinding the kernels to a smooth paste. Almond pastes are very popular in Europe and are known as marzipan.

Almonds are easier to store then other nuts. Ideal conditions are 4–7 °C (40–45 °F) with a relative humidity of 55–65%.

6.7.2.2 Brazil Nuts

Brazil nuts are grown in the tropics. They are used in chocolate bars as a whole nut or chopped. They can be chocolate enrobed or chocolate panned.

The trees are very tall, up to 48 m (150 ft) high. The fruits, on branches, are woody spherical cases that contain up to 24 nuts. When ripe, they fall to the ground and are collected. After collection, the fruits are opened and the nuts washed and dried. They are marketed in this form from the country of origin. The kernel is removed by mechanical means. The conditions for storage are similar to the conditions used for almonds. Brazil nuts are very resistant to infestation, because of their hard shell. For confectionery use, they are never roasted.

6.7.2.3 Cashew Nuts

The cashew nut tree (*Anarcardium occidentale*) is native to Brazil. The tree is an evergreen and grows up to 13 m (40 ft) high. The nut grows at the end of the fruit called a cashew apple. It is kidney shaped. The cashew apple is edible as a fruit but is very acid. The seed inside the cashew fruit is known as cashew nut. The roasted nuts have a soft texture and are mostly consumed as salted nuts. In confections, both nut and paste are used.

6.7.2.4 Coconut

The coconut (*Cocos* nucifera) is the nut of the coconut palm. The palm is a tree of the tropics that attains heights of up to 32 m (100 ft). The palm grows in sandy soil and requires large amounts of water, 200 cm (80 in.) per year or more of rainfall. The dried coconut meat is known as copra and is the source of coconut oil, which is used in great quantities by the baking and confectionery industries.

A major coconut product used in confections is known as desiccated coconut. It is produced by removing the nut from the shell and removing the thin brown rind from the nut. The pared nuts are washed to remove the "milk", after which they are passed through shredders, giving a milled product of various grades of fineness. After shredding, the product is steamed to destroy pathogenic organisms and to inactivate the lipases. The pasteurized meat is then dried in mechanical belt driers, which reduces the moisture content to less than 4%.

After drying, the desiccated coconut is put through several sieving steps to produce the four main grades; Extra Fine, Fine, Medium, and Coarse. In addition, cuts such as Flakes, Long Threads, Extra Fancy Threads, Slices, Chips, and Strips are produced and made available for specialized applications. Other coconut products made available are toasted coconut, moist sweet coconut, and creamed coconut.

High quality desiccated coconut should have a white color (unless toasted), be free from foreign matter, and uniform in granulation. The expressed oil should have a free fatty acid content of less than 0.1%. Coconut-containing confections can develop a soapy rancidity. This is attributed to residual lipase activity, which is the result of inadequate pasteurization.

Coconut products also can develop oxidative rancidity. Coconut confections exude oil in a thin film, which is subject to oxidation catalyzed by heat, light, and metals. Oxidative rancidity is less likely to occur than soapy rancidity.

Today, with much better quality, coconut products can be stored at temperatures between 4.5 and 7 °C (40–45 °F) and a shelf life of at least 6 months can be expected.

6.7.2.5 Hazelnuts or Filberts

The hazelnut is a popular ingredient in chocolate bars. The roasted nut flavor is synergistic to chocolate and the chocolate coating retains the nut's crisp texture.

The nuts are grown in Europe and Asia, with Turkey producing over 60% of the world's supply. Filberts are grown domestically, in the state of Oregon. A tree will yield between 9 and 45 kg (20–100 lb) of nuts, of which half the weight is kernel weight. The kernels vary in shape, size, and color.

Hazelnuts are roasted for confection and chocolate use. During roasting, the brown skin becomes detached and is removed by sieving and air suction. The result is a blanched kernel varying in color from off-white to brown depending on the degree of roast.

Under warm storage conditions, the nuts gradually shrivel. Hazelnuts, even when stored under cool conditions and controlled humidity, lose some of their quality. When nuts are given a slight roast, thereby reducing the moisture content to about 2%, stored in closed containers, and at temperatures between 4 and 7 °C (40–45 °F), at least 18 months of shelf life can be expected without quality loss.

6.7.2.6 Macadamia Nuts

Macadamia nuts are prized for their mild buttery flavor and crunchy texture. Major producing countries include South Africa and Australia. They are grown domestically in the state of Hawaii. The trees require abundant rainfall, porous volcanic soil, and almost year-long growing season. The tree is a subtropical evergreen. It grows to heights of 13 m (40 ft) and has dark-green leaves. The nuts begin as a series of tiny green buds, which develop into sprays of 300–400 white blossoms. Each spray produces four to eight nuts. When mature, the fruit resembles small limes. Beneath an outer husk is a hard, brown shell, which contains the macadamia nut kernel.

The tree flowers over a period of 4–5 months and thus, there are five to six harvests annually. Mature fruits fall to the ground and are collected. The harvested nuts are husked and then dried until the moisture is reduced to about 1.5%. This is done to separate the kernel from the shell. The shell is removed by passing the nuts between counter-rotating steel rollers, precisely spaced to break the shell.

The major macadamia product is whole, roasted, lightly salted, vacuum packed jars or cans. Their use in confectionery products includes brittles, and sugar and chocolate panned nuts.

6.7.2.7 Peanuts

The peanut (*Arachis hypogaea*) is a member of the pea and bean family and therefore, is not a true nut. When the flowers wither, the stalks bury themselves in the soil, and at the end of the stalks, the pods containing the seeds (peanuts) are formed. Peanuts are grown throughout the world, primarily for vegetable oil. In the United States, they are grown for food use. In round numbers, about half of the peanut crop goes into peanut butter, a fourth go into confections, and a fourth go into salted nuts. Since peanuts grow in soil, at harvest time, contamination of the nuts by soil organisms is very likely. It is therefore important that the peanuts, which have a moisture content of 30–40%, are dried to prevent mold growth, which can result in production of aflatoxins.

6.7.2.7.1 Peanut Varieties

Over the years, a number of peanut varieties have been developed, each being superior to others in some respects. Improvements involve higher yields, disease resistance, and ease of harvesting and shelling. There are four types of peanuts grown in the United States: the small Spanish type, used in peanut brittle; the large Virginia type, used for peanut butter, in shell consumption, and confections; the long Valencia type, which has two to four seeds per pod and is used mainly for in-shell consumption; and the Runner type. The Runner type is a high yielding variety. It yields two to three times that of either Spanish or Virginia types. Most of the equipment for harvesting, shelling, and processing is geared for this type of peanut. It is used for confections, peanut butter, and in-shell consumption.

6.7.2.7.2 Quality Differences

The quality of peanuts is impacted by the type, the variety, the growing area, and growing condition. Most of the quality differences in peanuts occur during harvesting, shelling, storing, and grading. The peanut, during its growth cycle, sets fruit for a period of up to 8 weeks. Therefore, at harvest time, each plant will have fully mature nuts, some half mature nuts, and some immature nuts. No matter which harvest time is chosen, the problem of mixed maturity is present. They will not only differ in maturity but also in size, moisture content, color, texture, oil content, and flavor.

A further consideration is the drying conditions. Drying must be done within a few days after harvest to prevent molding, yet be slow enough to allow enzymatic activity to develop maximum flavor. A third consideration is whether to store the nuts in-shell or shelled. Processing shortens the shelf life of peanuts. The shell of peanuts is a natural protection against insects and molds. Each step in the harvesting and processing removes protective layers and exposes the nutmeat to air, moisture, and microbes. Many processing steps rupture the cell, break the emulsion releasing oil, and exposing the nuts to enzymatic and oxidative rancidity. It is therefore desirable to store peanuts in-shell for as long as possible.

Apart from origin, age, maturity, and storage, the keeping properties are greatly affected by chopping and roasting. As with all nut type products, roasting and chopping will decrease shelf life. An unroasted nut/peanut will have a relatively long shelf life of a year or more. While roasting will give improved flavor attributes, there will be noticeable flavor deterioration within a month or two unless proper steps are taken (see Section 6.7.2.7.3). Chopping of nuts/peanuts causes release of oil over a greater surface area that will accelerate deterioration due to oxidative rancidity.

6.7.2.7.3 Storage

Peanuts are seasonal and semi-perishable. However, with proper preparation and storage conditions they can be available year round following certain conditions:

1. Use only nuts of known high quality.
2. Dry nuts to 4–5% moisture.
3. Seal the dry nuts in bags or drums that do not permit exchange of oxygen and flavors. Vacuum packaging or nitrogen flushing is preferred.
4. Store at 9 °C (48 °F) for immediate use, 0 °C (32 °F) for holding from season to season, and −32 °C (0 °F) for long-term storage.
5. Hold storage room relative humidity at 60% or lower and free of pronounced odors.

6.7.2.8 Pecans

Pecans are essentially an American nut, with minimal consumption in other parts of the world. The pecan tree grows wild in the Southeastern United States although many plantations are cultivated for commercial use. After harvesting, the nuts are cracked by machine. It is the practice to wet them before cracking, allowing time for moisture to penetrate to the kernel. This avoids breakage of the kernel. Kernels should be stored under refrigeration or frozen for long-term storage.

6.7.2.9 Pistachio Nuts

Pistachio nuts are better known for their appearance than their eating quality. They are pale green throughout, and are used in nougats often in combination with cherries and citrus peel.

The nut grows on small trees cultivated throughout the Middle East and Mediterranean countries. In the last 30 years, pistachios have been cultivated in California. The tree can grow under extreme dry conditions and very poor soil.

6.7.2.10 Walnuts

The walnut (*Juglans regia*) is one of the most widely used nuts in the world with China being the largest producer. Native to United States is the American black walnut (Juglan nigra), which has an excellent flavor, but limited commercial availability. Walnuts have a very hard shell, but the kernels have excellent flavor. The main nut-producing area in the U.S. is California. The tree grows to a height of 32 m (100 ft) and is cultivated in orchards. Where conditions are favorable, the nuts separate from the husk and fall to the ground. After collection, to prevent damage from mold and insects, they are washed, cured and dried. The drying is either by sun or mechanical dryers with air at 38–43 °C (100–110 °F). These conditions will prevent splitting and opening of the shell, which will occur with more rapid drying.

The mechanical cracking, cleaning, and sorting are complicated by the intricate shape of the nutmeat. Walnuts are sold as halves, quarters and pieces. In confections, halves are used for decoration of chocolates, quarters are used as centers, and pieces are used in chocolate bars and in caramel.

Black walnut trees are widely distributed in North American forests. The nut has a fibrous husk, which must be removed by machine. The remaining shell soon turns black, hence the name. The kernel is of high quality and excellent flavor.

Under warm and humid conditions, walnuts deteriorate rapidly. A confection should have a water activity not exceeding 0.5 if walnuts are to be included. If this is exceeded, the nuts become sour and later rancid.

Recommended storage conditions specify a temperature below 3 °C (38 °F) with an optimum relative humidity of 60%. The moisture content of the nuts should be between 2.8% and 4%. Storage properties can be extended with the application of sprays of edible oil containing antioxidants BHA and BHT.

6.7.3 Summary

The quality of all nuts is affected by harvest, handling and storage methods. To ensure good flavor, shelf life and freedom from infestation and foreign matter, processing and storage conditions must be carefully controlled. Delayed or incomplete drying after harvesting will encourage the development of molds, which may produce mycotoxin (aflatoxin) and cause breakdown of the natural fats in the nuts. This, in turn, will accelerate rancidity and produce off flavors. The moisture content of prepared kernels of all nuts should be below 4%.

Some nuts are much more prone to deterioration than others. Walnuts and peanuts are probably the most prone to deterioration, while almonds and Brazil nuts are relatively stable.

All nuts contain oils, which are of varying degrees of saturation. These oils are subject to oxidative rancidity, and deterioration is accelerated by warm storage, bruising or damage to the nuts. Storage conditions suitable for most nuts are 2–7 °C (35–45 °F) with a relative humidity of less than 55%.

With all nuts, the container used for storage must assure that no damage occurs. If nuts are stored in bags, they must be handled with care in order to prevent bruising. Bruising of nuts will result in expression of oil and cause discoloration. Prepared nuts, particularly if chopped or sliced, must be packed in rigid containers, preferably flushed with nitrogen to extend shelf life.

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Part II

Sugar-Based Confections

Compressed Tablets and Lozenges

7

7.1 Introduction

The pharmaceutical industry first produced lozenges and compressed tablets in the mid to late nineteenth century as a way to deliver a specific amount of a drug. Because drug quantities are often measured in milligrams or less, another powder was needed to provide the necessary bulk as a carrier of the active ingredient. The properties of this other (nonactive) powder define tableting ability in pharmaceutical applications.

The earliest such products used the lozenge process, where the drug was mixed with a paste (often containing starch, but also may contain gelatin or gums) to give a dough-like consistency. The dough was rolled into sheets and cut into individual lozenges, which were then dried in an oven. One problem with this approach was the interaction of the drug with water, which had potential negative effects. The manual nature of this process also led to variations in piece size, shape and form.

In a later development, compressed tablets were developed where the powdered raw materials were mixed together, poured into a mold and then compacted with a die punch. The high pressure caused the individual particles in the powders to bind together in a tablet. This process eliminated many of the problems with the lozenge process.

The development of compressed tablet candies followed tablet developments in the pharmaceutical industry, with the introduction of several confectionery brands in the early 1900s. Since then, numerous compressed tablet and lozenge-type candy products have been developed for the market place. These candies typically use either sucrose or glucose (dextrose) crystals as the primary particles, although tablet and lozenge candies can be found with sugar polyols (e.g., sorbitol) as well. Binders, the materials that hold the particles/granules together, typically include corn syrup and a hydrocolloid, such as gelatin or gum arabic.

Some materials, like glucose (dextrose), sorbitol, maltitol and isomalt are suitable for direct compaction as long as the particle properties (size, distribution, density, water content, etc.) are appropriately chosen. Other materials, particularly sucrose, generally need prior treatment, wet or dry granulation, to develop an acceptable powder for compaction. Wet granulation is the process of aggregating individual particles or crystals into granules that can be more easily compacted. In this case, the binder is applied to the powder to make a paste, which is then dried and ground back into a powder. The binder holds the granules or aggregates together and the applied pressure to form the tablet causes the aggregated granules to bond together to form a hard tablet. Alternatively, dry granulation (or dry

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slugging) can be used to prepare a powder for the tablet press. The primary particle is first pulverized and then mixed with the lubricant before being compacted into pellets. These pellets are ground and sized to produce a powder suitable for compressing into tablets.

The microstructural characteristics of tablets are dependent on the nature of the granulation (base particles, binder used, water content, etc.), the type of press, and the compaction conditions (compaction pressure, compaction speed, etc.). Even environmental conditions (temperature, relative humidity) affect granulation flow properties and tablet formation. Sufficient pressure is applied so that the powder particles physically rearrange and/or chemically bond together to form a hard tablet. Under pressure, particles rearrange in such a way that smaller ones fit more closely within the interstitial spaces between the larger ones. Certain types of particles may also deform (either reversibly or irreversibly depending on the nature of the particle) to allow them to move more easily within the matrix. Fragmentation of particles under the applied pressures may also promote rearrangement. Bonding between particles can occur due to electrostatic forces, capillary forces, or the particles could even melt under high pressure, flow together, and then solidify with solid bridges when the pressure is released.

Because very little water is used to make the powder for compaction (or that water is dried off after wet granulation), the water content of a tabletted candy is typically very low, less than 0.5%. The exception to this is when dextrose monohydrate crystals are used to make the tablets. For each molecule of dextrose, one molecule of water is incorporated into the lattice. This 1 to 1 ratio on a molar basis turns out be about 9% moisture on a mass basis (as measured for example by Karl Fischer titration). However, because this water is all bound with the crystal lattice, it is not free to associate at particle surfaces and does not induce stickiness problems.

The hardness of a tablet depends on the nature of the powdered material, which of the above mechanisms holds the particles together, and the applied conditions. Time under pressure, the pressure exerted and temperature of compaction all influence hardness, and therefore the dissolution ability, of a tablet candy.

Lozenges, on the other hand, are not formed under pressure so particle rearrangements do not occur. Lozenge or wafer-type products are formed by mixing dry powder (e.g., confectioner's sugar) with liquid binder to form a paste. When the liquid binder is added to the powder, some of the sugar dissolves as liquid and solid components of the paste equilibrate. This paste or dough is then formed (i.e., sheeting and cutting, extrusion, etc.) to make individual pieces, which are then dried into hard lozenge candies. When water is removed during drying, sugar crystallization forms bridges between particles, contributing to a hard texture. The physical characteristics of lozenges (e.g., hardness) are influenced by numerous parameters, including the type of base particle used, the nature of the binder (how much used and its composition), the water content of the dough, and the final water content of the dried product.

Compressed tablets are, in general, harder than lozenges, although a wide range of textural characteristics can be found for both candies. Some tablets break apart readily in the mouth, whereas other tablets are extremely hard. Certain types of hard tablets are often called "hard" candy even though they are quite distinct from the glassy candies typically called hard candy (see Chapter 8). The physical characteristics of compressed tablets are influenced by both the ingredients and the process conditions used to make the candy.

Tablets and lozenges are typically quite low in water content and therefore, have low water activity (<0.5) and fairly long shelf life. They are also comprised primarily of crystals so they are not very hygroscopic unless stored at humidity above the deliquescent point of the particle (about 80% for sucrose). This is particularly true for sucrose and dextrose-based candies. Some polyol-based tablets (i.e., sorbitol, xylitol) can be quite hygroscopic, so a lower RH environment is required. The main issues with shelf life of tablets and lozenges are loss of flavors or rancidity. Over time, volatile flavors can diffuse out of the candy leaving a product with reduced flavor impact. Flavors such as mints can oxidize during storage, developing an off-flavor. At times, tablets or lozenges may also pick up off-flavors from the surroundings and thereby, lose quality.

7.2 Formulations and Ingredients

Some typical formulations for tablet and lozenge candies are given in Table 7.1. The bulk of a compressed tablet or lozenge candy is the base material. This is the powdered sweetener that is either compressed into a tablet or held together by a binder to make a lozenge candy. Depending on the nature of the sweetener used, a tablet formulation may also include a binder to hold the particles together prior to compression. Tabletted candies contain a lubricant, which keeps the powder from clumping prior to compression and the tablet from sticking to the die once it has been formed. A disintegrant may be used to help in breaking down the tablet during consumption or use. Flavors, high intensity sweeteners, colors and acids are also added to taste. Active ingredients, like vitamins or other functional ingredients, may be added.

7.2.1 Base

The tablet base, which was initially the vehicle for delivering an active compound in the first pharmaceutical tabletted products, makes up the bulk (90–95%) of a candy tablet. In confections, the most common base materials are sucrose, glucose (dextrose), and sorbitol. Glucose can be used either in the monohydrate crystalline form or as a blend with maltodextrins. Recently, sugar-free tablets have been made from isomalt, mannitol or xylitol powders as well as from microcrystalline cellulose. Powdered gum base can also be used for tableting. Choice of base depends on the desired characteristics of the final product, its compression characteristics, and the cost. If an active component is to be used in the compressed tablet, the capacity of the base (amount of active ingredient that the base can hold), and potential reactions with the base must also be considered. Particle size of the active ingredient must be close to that of the binder to prevent stratification and separation.

Table 7.1 Typical formulations (%) for tablets and lozenges

Ingredient	Direct compaction tablet	Wet granulation tablet	Lozenge
Base	98	90–95	90–95
Binder syrup	–	2–8	2–8
Glycerin	–	–	0–3
Acid	0–1.0	0–1.0	0–1.0
Lubricant	0.5–1.0	0.5–1.0	–
Flavor	0.5–1.0	0.5–1.0	0.5–1.0
Color	0.1	0.1	0.1

The type of base used determines the conditions required for tablet processing and the final characteristics of the tablet. Some types of bases (i.e., glucose and sorbitol) can be compressed directly as long as particle size is correct, whereas other bases (sucrose, isomalt, etc.) generally must be granulated prior to compression. Sucrose typically undergoes a granulation process to ensure proper compression into tablets, although a direct compaction version has been developed (Vink, personal communication). The nature of the granulation fed into the tablet press is determined by the compression properties of the base.

In the pharmaceutical industry, there is growing interest in mixing base materials, often called coprocessed excipients for direct compaction. The intent is to mix a ductile material (cellulose or amorphous sugar) with a brittle material (sucrose) to help hold the tablet together. For example, a directly compressible sucrose powder is available that contains sucrose crystals co-processed with a small amount of a polyol. The polyol moderates the compression mechanisms such that sucrose crystal can be directly compacted into a tablet with acceptable properties.

7.2.2 Binder

In a tablet made by the granulation method, a binder is needed to ensure proper press operation. The binder holds the individual granules of base together for compression. In a lozenge, the binder is the glue that holds individual particles together after drying. Common binders in confections include glucose syrup, maltodextrin, gelatin, natural gums (i.e., gum arabic, tragacanth, etc.) or some combination of these. Binders are typically added at levels between 2% and 8% of the final product. Choice of binder depends on the type of base used and the desired texture/strength of the product, whether a tablet or lozenge.

Different binders deliver different properties, particularly in lozenges where the binder is the primary mechanism of holding particles together. Gum arabic typically produces a brittle lozenge, tragacanth gives a hard and smooth lozenge, and gelatin gives a more elastic texture. Combinations of binders give properties intermediate of the individual binder and are often used to reduce costs.

7.2.3 Lubricant

In compressed tablet confections, a lubricant is also needed to ensure proper press operation. The lubricant serves several important purposes. Initially, the lubricant must act as a glidant, to aid flow of the powder material into the press and ensure uniformity of the final product. The lubricant must also act as an anti-adhesive, to prevent the base from sticking to the punch (for compression). Finally, the lubricant helps to ensure that the tablet releases easily from the press without sticking to the die walls.

In confections, the most common lubricants are magnesium stearate, calcium stearate, and stearic acid. In some tablet candies, hardened vegetable fats and mono- and diglycerides serve as lubricant. Choice of lubricant is based on the characteristics of the final product, efficiency of the lubricant with the chosen base and binder, and reactivity with the other components in the pressed tablet. In some systems, higher levels of calcium stearate are needed to give the same lubrication compared to magnesium stearate or stearic acid. However, magnesium stearate and stearic acid tend to be more reactive than calcium stearate, particularly in tablets containing flavors that are prone to oxidation. For example, magnesium stearate can lead to a soapy off-flavor, particularly when made from an animal fat.

Lubricants are added at levels between about 0.5% and 1% of the final product, at a sufficient level to coat the surface of the granulation. Particle size and density of the lubricant, in addition to mixing time and intensity, are factors that affect the ability of the lubricant to coat the granulation. Although it is important that the lubricant coat the granulation, this lubricant coating interferes with bonding between the particles and thereby, decreases hardness of the tablet. For this reason, the lowest level possible for lubrication purposes should be used.

7.2.4 Disintegrant

In some cases, it is desirable to have a product that disintegrates quickly, either upon consumption or, for example, when dropped in a glass of water. Certain types of starch or a soda/acid mix (citric acid and sodium bicarbonate) may be used to help break down candy tablets upon contact with water or saliva. For example, pre-gelatinized (cold swelling) starch swells when it comes in contact with water, breaking the bonds between the particles of the granulation and leading to disruption of the tablet. The combination of citric acid and sodium bicarbonate provide another disintegrant mechanism. They react upon contact of the tablet with water, causing release of carbon dioxide gas and disintegration of the tablet. Tablets that fizz when dropped in water (Fizzies or antacid products) disintegrate rapidly based on the soda/acid system. However, the acid/bicarbonate system is prone to moisture uptake, so their use is somewhat limited.

7.2.5 Acids

A variety of acidulants can be used in pressed tablets, although the main organic acids used are citric and malic acids because they are available in powder form. When using citric acid, tableting must take place at very low relative humidity since the powder is quite hygroscopic. Acid is usually added at 1% of the product mass, although some tablet products contain higher acid content to provide an intensely sour effect.

Acids must be used with some care since they can cause problems. For one, the candy will become more hygroscopic, with a reduced shelf life. Also, the acid may “break” the lake, leading to spotted or mottled effects, particularly for some red and blue lake colorings.

7.2.6 Flavors

The choice of flavor type and level in tablets and lozenges depends on numerous factors. The type of base (whether sucrose, glucose or polyol) has a significant impact on flavor sensation. The sweetness (or lack thereof) and cooling sensation that comes from glucose and most polyols are certain to impact flavor sensation. Furthermore, the compaction density and thus, the rate of dissolution in the mouth, influence the rate of flavor release and consumer perception. Mints and spice flavors were most common for tablets in the past due to their more potent flavoring, although sour fruits with a potent acidulant are now also quite common.

Both liquid and spray dried flavors are used in compressed tablets. However, the effects of the flavor solvent must be considered when using liquid flavors. Oil-based flavors (mints, spices, etc.) can be added in liquid form with no problem. However, solvents like propylene glycol would impede lubricant functionality and result in excessive stickiness of the granulation; thus, spray-dried forms of these flavors are preferred despite their higher cost and higher use levels. Either liquid or solid flavors can be used in the lozenge process.

Flavor levels are generally quite high (0.5–1%) in compressed tablet confections since the slow dissolution of the tablet in the mouth retards flavor release. The exception to this is mint and sour fruit flavors, which give more rapid release. To prevent flavor losses during blending and storage, a problem compounded by the porous nature of the tablet, encapsulated flavors are often used. Spray dried flavors generally lose some potency when the flavor particles are crushed during pressing, but retain flavor better during storage.

Flavor interactions with other tablet components, primarily the lubricant, can lead to problems with compaction. Interactions between flavors, particularly liquid flavors, and lubricant decrease the ability of the lubricant to promote uniform flow and may lead to problems during compaction. Specifically, water or glycol-based flavors can cause the granulation to become sticky and impede flow into the press. In severe cases, the granulation can stick to the punch faces, causing a problem called picking, or misshapen surfaces. High levels of oil-soluble flavors can also cause a reduction in lubricant efficiency, leading to scoring of the side of the tablet as it is ejected from the die. Liquid flavors (nonmint) that contain triacetin or medium-chain triglycerides as their solvent system will provide less reduction of lubricant efficiency than oil-based flavors at a high level.

Fairly high levels of flavors are also used in lozenge candies because of the volatile loss during the drying process. Significant flavor loss, particularly with volatile flavors (e.g., peppermint), occurs during drying. Encapsulated flavors may reduce flavor loss during drying.

7.2.7 Colors

Either dyes or lakes can be used, depending on the process for making tablets or lozenges. In lozenges and wet granulations for tablets, soluble dyes can be used because there is sufficient liquid added initially to disperse the color. In lozenges, color solution is added prior to making the wet granulation. However, tableting by dry granulation or color addition in direct compaction generally requires the use of lakes, in dry form. Very fine lake colors are used to coat the granules. If the granulation is too large, however, the large granules may get crushed and the lake may not be fully dispersed. This leaves white, colorless regions and a speckled or white spotted appearance.

Many exempt or “natural” colors act as dyes and can be used in place of dyes. Carmine and some of the new matrix colors (natural pigments) can replace lakes in direct compression. Color specks and even edible glitter can be incorporated in dry granulation or direct compression for a speckled effect and visual differentiation.

The actual hue for a color depends to some extent on processing conditions, particularly compression pressure. Since the bulk density of the piece changes with applied pressure, the specific hue of given color may vary somewhat.

7.2.8 Actives

Compressed tablet candies can contain up to 25% of active ingredients, although this depends to some extent on interaction effects in compression. Common active ingredients include vitamins, minerals or other functional components like breath fresheners. The advantage of delivery of some of these compounds in tablet form is that there is minimal heating and thus, minimal thermal degradation of the active ingredient. The lack of water is also beneficial to stability of many active ingredients. Some actives are easier to incorporate into the compressed tablet matrix without causing problems, such as excessive softening.

7.3 Processing

Lozenges or wafer candies are made by combining a powder together with a binder, without the use of high pressure to fuse particles (Figure 7.1). In this case, the binder (sometimes called a mucilage) is used to simply "glue" the solid particles together in the wafer form. Once a paste or dough has been formed, lozenges or wafers can be shaped by sheeting and cutting, or they can be extruded and cut to the desired size. Once shaped, the lozenges are dried to a final moisture content less than 1%. The lozenge process is essentially the same process used in making a wet granulation for a tablet press.

Tableted confections are made by compression of a powder in a tablet press. The powdered or granulated raw material is filled into a cavity or die, compressed between punches, and then released from the mold, as shown schematically in Figure 7.2. Controlling the size and shape of the cavity as well as the applied pressure governs the nature of the candy product. In general, higher applied pressure leads to harder tablets, although different powdered materials have their own

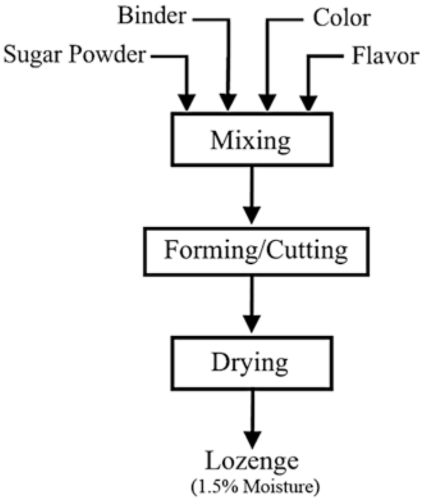


Figure 7.1 General steps for lozenge process

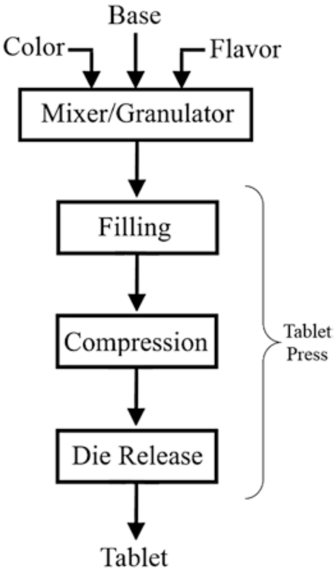


Figure 7.2 General steps in compressing a candy tablet

unique response to compression, particularly when mixed with the various ingredients (flavors, lubricants, etc.) that go into a tablet candy. Particulate characteristics like density, particle size, and shape also influence tablet characteristics. Thus, careful preparation of the powdered materials prior to compaction is essential for control of the desired tablet properties.

7.3.1 Lozenges/Wafers

The mixing of ingredients for lozenge production is relatively simple compared to the steps necessary for tablet production. To make a lozenge candy, the binder ingredients are first blended together, with the binder slowly added to the powdered base until a dough-like consistency has been attained. After the dough is formed and cut, the lozenge pieces are dried in an oven (Figure 7.1).

7.3.1.1 Dough Mixing

A lozenge binder is made by mixing corn syrup, water, and a hydrocolloid (i.e., gelatin, gum arabic, or combination). The solids content of the binder may be about 40–50%. To make a dough consistency, about 15–20% binder is added to the lozenge base (e.g., powdered sugar). This gives a dough with a water content of about 5–10% and a water activity above 0.75. The dough produced in this way is malleable and easily formed into the desired shapes, yet holds its shape during drying. If too much binder is added, the dough becomes sticky and is hard to shape, whereas too little binder results in dough that is crumbly and too firm to manipulate.

Dough mixers for lozenge processing are typically large batch mixers, with powerful motors to completely integrate the binder into powdered base material. Z-blade mixers can be used for mixing dough, although other mixer elements may be used as well.

7.3.1.2 Forming and Shaping

Once the dough is developed, it must be quickly formed and cut to the desired shapes before it loses too much moisture to the environment and becomes hard. A common method of forming lozenges starts by forming a sheet with the desired thickness by forcing it between two rollers, a process sometimes called calendaring. The sheet of dough is collected on a conveyor that removes the sheet at the same speed as it is formed from the rollers. Cutter heads (cookie cutters, drop frame rollers or rolling and scoring cutters) then cut the dough into the desired shapes. In some cases, the cutters have spring release mechanisms to ensure that the cut pieces do not get stuck in the cutters. The webbing material from between the candy pieces is separated by off-set conveyors and recycled back into the mixing device for reuse. Careful control of ingredients and processing conditions are needed to ensure that the dough does not stick to cutting or processing equipment (knives, rollers, conveyors, etc.).

Alternatively, the sugar dough can be extruded into the desired shape and cut to the desired size as it exits the die. The dough is fed to a forming extruder where it is forced through a die with the desired candy shape. As the dough exits the die of the extruder, a knife cuts the stream of dough into a candy piece with the desired thickness. The pieces are collected in shallow trays or on a conveyor and taken to the oven for drying. Often products like sprinkles, confetti and nonpareils are processed in this method.

Products like Conversation Hearts and other wafer candies often have a logo or saying imprinted on one side, sometimes in a color different from the candy color. Such lettering may either be embossed (raised lettering) or, more commonly, debossed (indented lettering) with the appropriate punch design as the pieces are cut out of the dough sheet. Lettering can be printed in edible ink on the surface of a candy in a flexographic rubber roller process, where the lettering is applied to the sheeted candy in a sequenced operation prior to stamping out the piece. The ink is made of edible colors and shellac in a solvent (ethanol is the most common solvent, but some water-based inks are now available).

7.3.1.3 Drying

The formed candy pieces then go through a drier to remove water. Drying must start slowly, with air temperature initially only 24 °C (75 °F), to reduce shrinkage and cracking. Final drying (or stoving) is done with air at 35–40 °C (95–104 °F) and relative humidity less than about 50% to promote drying. Complete drying may take up to 12–15 h to attain the final moisture content. The candy pieces are often turned once during drying to expose both surfaces equally. Once the lozenge candies are dried to about 1.5% moisture, they are cooled and then ready for packaging.

7.3.2 Tablets

Compressed tablet candies are made by forming a compressible powdered granulation and then compressing the powdered material under high pressure in a tablet press (Figure 7.2). Careful attention to the properties of the powder fed to the press is necessary to efficiently produce candy tablets with minimal defects.

In most cases, some preparation of the base and other ingredients is necessary to ensure that the powder flows easily through the press and that the desired compaction takes place. For example, if a granulated sucrose powder (table sugar) was compressed in a tablet press without prior treatment, it would not form a suitable tablet confection. The large (≈400 μm) crystals in granulated sugar are not sufficiently compactable and do not form a cohesive tablet with the desired strength. Even finer powdered sucrose does not compact directly due to the response of the sugar crystals to compaction pressure. To prepare sucrose for tableting, it must first be pulverized to smaller size and then processed with other ingredients before compression. The most common method for preparing sucrose for tableting is the wet granulation method, where a dough is made from binder and sucrose (similar to lozenge processing) and pressed or extruded through a screen. The dough is dried, ground and sieved to proper particle size before being blended with other ingredients (color, flavor, lubricant, etc.) and then fed to the tablet press. However, each base material has different requirements dependent on its properties and compression characteristics.

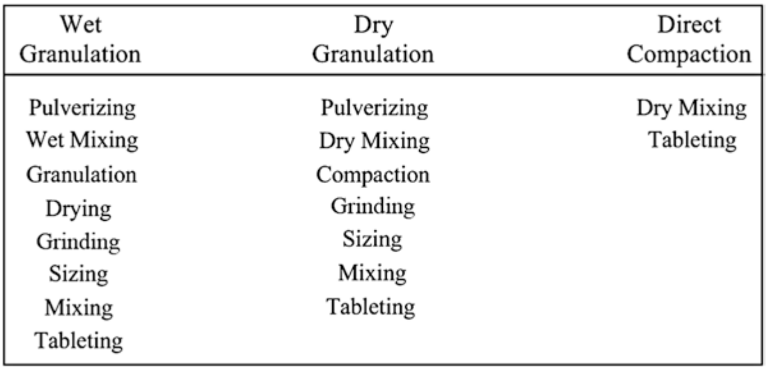
7.3.2.1 Ingredient Preparation

To help ensure that the powder is suitable for compaction, certain preparation steps are typically needed. Powder preparation may be done in the manufacturing facility or may be done by an ingredient supplier. The three options available to the tablet maker are wet granulation, dry granulation, or direct compaction. The steps involved with each process are outlined in Figure 7.3.

7.3.2.1.1 Wet Granulation

In wet granulation, table sugar must first be pulverized, typically by grinding in a mill (Fitzmill, Tornado mill, Micropulverizer, etc.), to reduce particle size. Grinding should continue until the powder is sufficiently fine. To this ground powder, the wet ingredients like binder (e.g., glucose syrup) and any liquid colors would be added. Since the amount of powder far outweighs the amount of binder, high torque mixers are required to ensure good mixing and a thick dough-like

Figure 7.3 Process steps for ingredient preparation for tablet production (Adapted from Vink 1996)



Wet Granulation	Dry Granulation	Direct Compaction
Pulverizing	Pulverizing	Dry Mixing
Wet Mixing	Dry Mixing	Tableting
Granulation	Compaction	
Drying	Grinding	
Grinding	Sizing	
Sizing	Mixing	
Mixing	Tableting	
Tableting		

product is the result. Often, dough mixers or sigma-blade mixers would be used for this purpose. The dough would then be squeezed through a screen to form a granule. A paddle or bar forces the dough through the screen, which can be either rotary or oscillating type. In batch processing, each of the above steps would be performed in a separate piece of equipment. The candy mass would be moved either manually or by conveyor from one piece of equipment to the next.

The wet granulated product may contain anywhere between 3% and 5% moisture and should be dried to 0.2–0.8% moisture. Static bed driers, fluidized bed driers or a continuous rotary (kiln) drier can be used to remove moisture. The dried product must then be ground and sieved to the correct size for compaction. Temperature control during drying is important to minimize negative changes in the granulation. For example, if gelatin is used as the binder, temperatures above the point where degradation occurs must be avoided in the drying stage of wet granulation, so air temperatures should be less than about 93 °C (200 °F).

At this point, it is necessary to ensure uniform particle size in order to prevent problems with control of the compaction step and the final product characteristics. The dried product is ground in a mill until it reaches the desired particle size distribution. The optimal size range for tableting depends on the powdered material being compacted, among other factors. The nature of the other ingredients used in the formulation also influences the optimal size range. No single standard size distribution recommendations cover all types of granulations and base materials. For a sucrose powder based on wet granulation, a standard recommendation might be that 100% of the particles pass through a 20-mesh sieve (840 μm) and at least 90% is retained on a 60-mesh sieve (250 μm). For a sorbitol product, a distribution of sizes between a 60 and 100 mesh size (150–250 μm) gives good compaction results. In all cases, it is important to have somewhere around 10% fine particles that fit into the interstitial spaces between the larger particles, helping to hold them together and give strength to the tablet.

Once the granulation has been ground and sized, all other ingredients (flavor, dry color, acid, any active ingredients and the lubricant) are mixed in with the granulated base material. Typically, liquid flavors are added first to provide for uniform distribution. Dry colors and acids are added separate from liquids to avoid spotting. The lubricant is added last to ensure complete coating of all particles. This mixture now forms the free-flowing base for the tableting step.

Several processes are available for what might be called “all-in-one” wet granulation, where all the steps leading to formation of a granule for grinding are done in a single unit. For example, a fluidized bed granulator can be used to prepare a wet granulation for compaction. An air stream fluidizes the individual particles and the wet binder is sprayed onto them. Agglomeration of individual particles forms a granule, which is then dried by the warm air fluidizing the particles. Lubricant and flavor may also be added to the dried granules in the fluidized bed. Another efficient process for wet granulation is extrusion. Extruders that combine wet mixing, granulating, drying and final blending in a single unit are available. For example, a twin screw extruder can be used to blend the powder with the wet ingredients, dry the mass by pulling a vacuum within the extruder, and then blend the dry ingredients to make the final granulation. Subsequent screening may still be necessary prior to feeding the tablet press. The continuous extrusion process is extremely efficient; however, fairly high product throughputs (up to 2,500 kg/h; 5,500 lbs/hr) are needed to make the process economical.

7.3.2.1.2 Dry Granulation

In dry granulation, the first step of the process is to pulverize the base material, just as in wet granulation. A small amount of dry binder (e.g., gelatin) is added after pulverizing – the granulation and drying steps found in wet granulations are not needed in this process.

After the pulverized base has been mixed with the binder, the mixture is compacted into pellets. This may be done in a roller compactor, where the powder is fed into a narrow gap between two pressure rollers, or by slugging, where the powder is formed into tablets at slow speed and high pressures. The compacted pellets are ground into smaller size in a communitor (or oscillating granulator) and sized prior to addition of flavor, color, acid, active ingredients, and lubricant. Addition of these components is done in the same order as in wet granulation. The same granulation size distributions as in wet granulation apply here as well. The free-flowing mixture is then ready for tableting. Sucrose, glucose, lactose, microcrystalline cellulose, and sorbitol are examples of materials that can be dry granulated.

7.3.2.1.3 Direct Compaction

In direct compaction, the base material particulates possess desired properties (fracture, deformation, etc.) for making a suitable candy tablet. These bases generally do not require granulation to produce acceptable tablets. However, not all base materials have these properties. Sorbitol powders can be compacted directly without pretreatment due to the nature of sorbitol crystals. The γ-polymorph of sorbitol has the best direct compaction properties and is not as hygroscopic as the other forms. Lactose, lactitol and mannitol powders can also be directly compressed into a suitable tablet. Amorphous corn syrup powders can also be directly compacted. In fact, spray-dried materials such as glucose syrup solids (high DE) and sorbitol mixtures make excellent bases for direct compaction because the granules are spherical and have lubricant only on the outside surface. When compacted, the nonlubricated center of the granule provides good adhesion and results in stronger bonds between particles.

In another form of direct compaction, a prepared base material is purchased from a supplier and the candy manufacturer simply adds the desired colors, flavors, acids, active ingredients, and lubricant prior to tableting. The advantage to the candy manufacturer is the ease of use and simplicity of the process. However, because the supplier has performed the preparation steps (wet or dry granulation), where necessary, the cost of the pre-made base is typically greater than that of the raw materials.

7.3.2.2 Powder Conveyance

In preparation of the base prior to and during tableting, it is important that no changes take place during conveyance to the press. For one, environmental conditions must be carefully controlled. Since many powders are hygroscopic, relative humidity in the air must be sufficiently low that moisture pick up is not a concern. If relative humidity is too high, the powder (particularly for sorbitol and dextrose monohydrate) quickly loses its free-flowing capacity as the surface of the particles become sticky. This can lead to numerous problems during tableting. Temperature may also be a concern for certain base materials. Melting of the lipid components may be a problem at elevated temperatures. Amorphous base materials may also become sticky with increased temperature.

An important property of the granulated powder fed to the tablet press is its particle size distribution. This determines how well the particles squeeze together under pressure to bond into a tablet. In general, a fairly uniform distribution of sizes is best, with sufficient "fines" to fill in the interstitial spaces between larger particles. Air conveying can cause classification of sizes that cause problems with tableting (weights off and thickness differences). Thus, bucket conveyors are generally a better bet for ensuring that the powder is fed uniformly into the hoppers. Screw conveyors or air conveyance may also be used but must be carefully controlled to minimize particle degradation.

Although numerous factors affect the flow characteristics of powders, the Carr's Index (or Carr's Compressibility Index) is often used as a quick check on these properties. The Carr's Index (CI) is defined as:

$$CI = \frac{(V_B - V_T)}{V_B} 100 \tag{7.1}$$

where V_B is the volume of the powder allowed to settle freely while V_T is the volume of that powder after controlled tapping to allow it to settle further. The Carr's Index can also be written in terms of bulk densities (mass per unit volume of the powder):

$$CI = \frac{(\rho_T - \rho_B)}{\rho_T}100 = \left(1 - \frac{\rho_B}{\rho_T}\right)100 \quad (7.2)$$

where ρ_T is tapped bulk density and ρ_B is freely settled bulk density.

The CI provides insight into how well a granulation will flow and compact. As a rule of thumb, CI values between 15 and 25–30 give good flow properties and compact well. CI values below 15 will flow well but will not compact very well. CI values above 25–30 will compress well, but will cause flow problems when feeding the press. Factors that affect CI include particle size distribution and mean size, particle shape and moisture content, especially surface moisture. This latter parameter depends to a great extent on the relative humidity of the environment, which should be controlled to ensure proper flow properties.

7.3.2.3 Compression

Once an appropriate powder has been prepared, it is ready for feeding to the tablet press. For the best tablet production, both environmental conditions and tablet press operating conditions must be carefully controlled (Vink 1993).

7.3.2.3.1 Tablet Press

Once the dry powder materials are ready, tablets are formed by compression of the prepared base in a die press. A tablet press involves a series of steps, with powder flowing into the unit through a hopper and tablets exiting the chute after compression (Figure 7.4). First, the granulation is fed to the press and flows into the die (Figure 7.5a) where the weight of powder in the cavity is adjusted to give the desired weight of tablet (Figure 7.5b). The powder is then compressed between two punches under high pressure to form the tablet (Figure 7.5c), which is then ejected from the press, usually by raising the bottom punch to push the tablet out of the press (Figure 7.5d). Typically, these operations take place in a continuous series of events in a rotary device, where movement of both bottom and top punches is controlled by a set of cams and tracks (Figure 7.6).

To control product piece weight, it is necessary to control the flow of the granulation into the

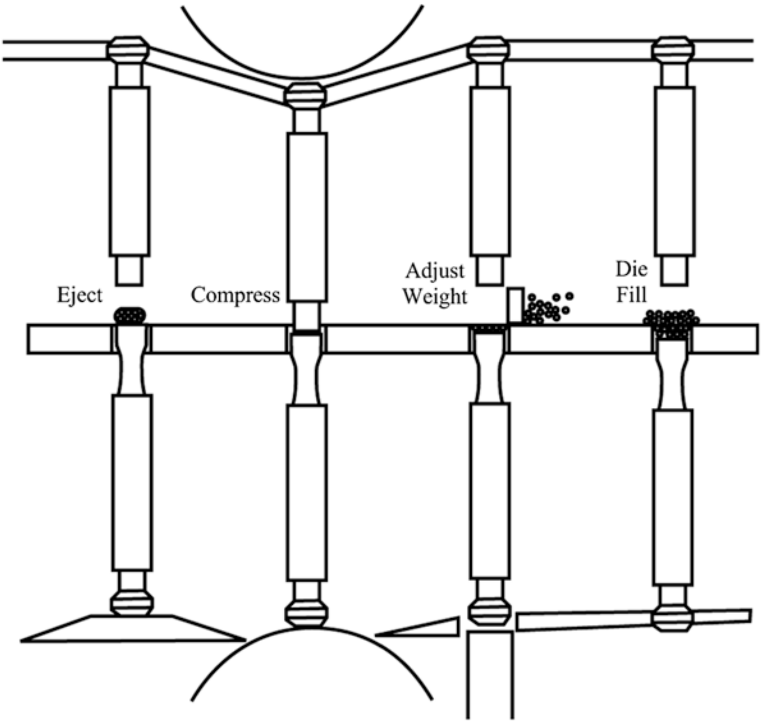


Figure 7.4 Operating steps of a rotary tablet press (From Vink 1996)

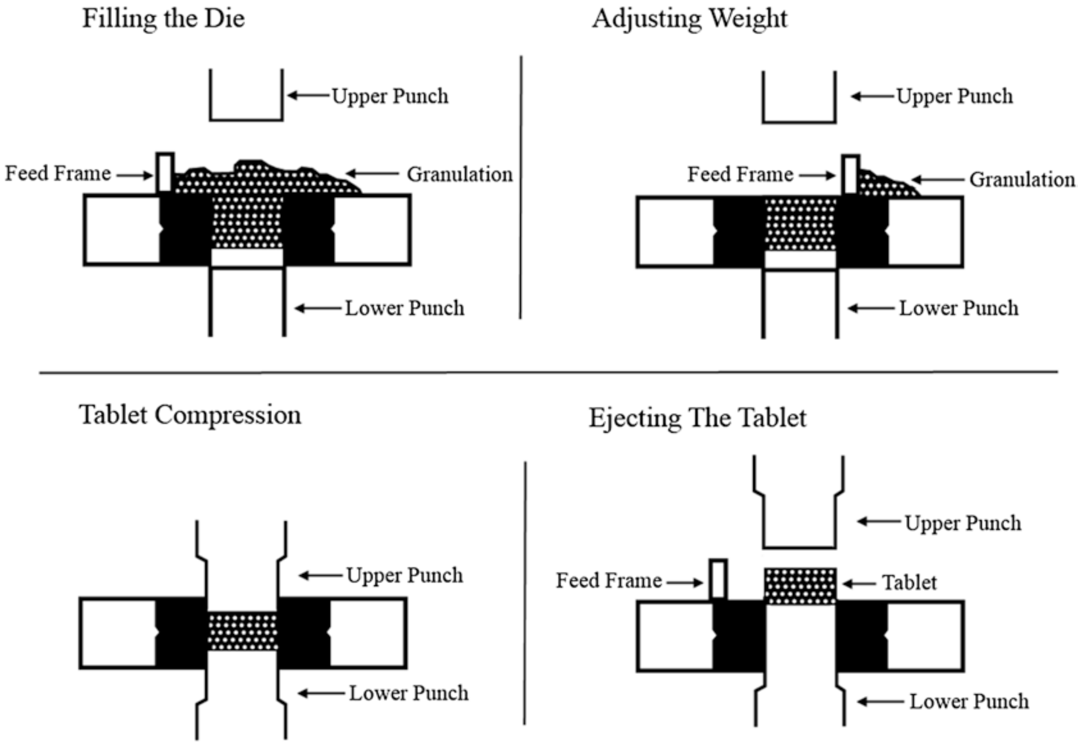


Figure 7.5 Detailed operations of a tablet press (From Vink 1996)

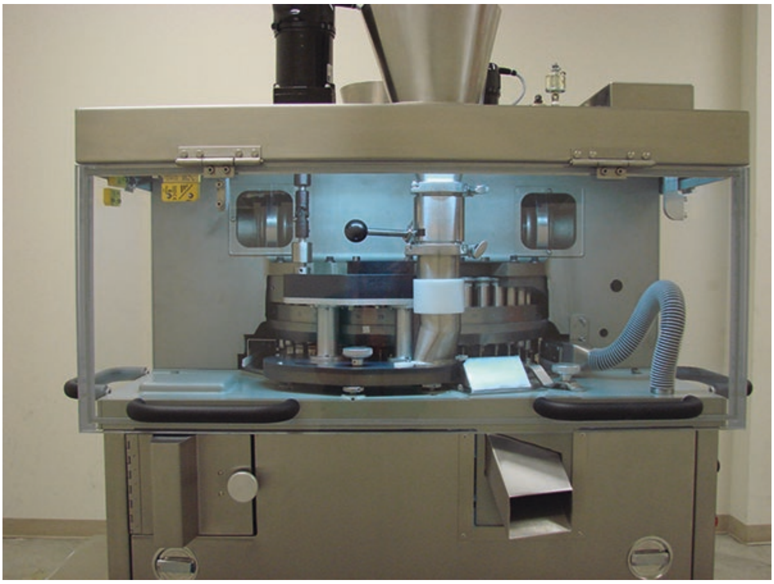


Figure 7.6 Rotary tablet press, model Stokes 328 MFA (Courtesy of Compression Components and Service, LLC)

press (Figure 7.5a). It is absolutely essential for good press operation that the powder be completely free flowing. Further, if the base material has not been mixed properly and does not have uniform bulk density, control of base flow will be difficult and problems in operation of the press will be encountered. Either controlled gravity flow or a forced flow feeder can be used to ensure proper filling of the cavity in the die press.

Once the die has been filled with a base material, the bottom punch moves into the correct position to set the weight of the piece and a scraper clears excess base material off the shelf (Figure 7.5b). This step ensures that the same weight of base material is compressed in each stroke. Once the die has been properly filled, the bottom punch is positioned at the correct level and the top punch enters the die cavity (Figure 7.5c). The tablet is compressed between the two punches with the force controlled by the distance set between the punches (set by the rollers that control the punches), the depth of fill, and the override pressure, which is set on the press. Compression forces are applied in the normal direction of the punch movement (vertically) with a resultant force in the normal direction to punch operation. The dwell time of the tablet under compression must be controlled to ensure proper bonding of the particulates. Typically, dwell time is governed by the operating speed of the press, but usually falls within 50–500 ms duration.

After the tablet has been compressed, the top punch is pulled away and the bottom punch is raised to eject the tablet from the cavity (Figure 7.5d). Candy pieces are then collected from an exit chute, and sent on for packaging.

To set the tablet press, trials are performed at different applied pressures and the tablets are weighed to ensure the proper weight is attained. If adjustments are necessary (weight too high or low), the applied pressure and the cavity fill level are adjusted until product with the correct hardness and set weight are produced consistently. Tablet thickness is governed by the amount of powder fed into the die (fill weight) and the pressure applied during compaction.

Many modern tablet presses have the capability of producing multiple layers or a layer within a layer. Sequential feeding zones and compression steps allow production of these more complex tablets.

The shape of the candy tablet is, of course, dependent on the shape of the die punches used to compress the tablet, with a wide range of sizes, shapes and thickness available. However, some shapes are easier to make because of the nature of the applied forces during compression. Discs are the easiest to compress because the forces applied in the punches are primarily normal to the shape of the tablet and the forces are uniformly applied across the entire piece. As the shape deviates more and more from disc-shaped, the distribution of applied forces leads to different extents of compaction across the tablet. This variation across the piece may lead to nonuniform products.

Text can be applied to the surface of the tablet through special design of the die punches. For example, embossed lettering on the tablet piece is created by making a die with the reverse lettering on the surface. As the punch compresses the powder, the raised lettering on the punch creates the reverse lettering indentation on the tablet. Debossed lettering may be made with a punch that has indented lettering on the surface.

7.3.2.3.2 Compaction Pressure

To compress a tablet, a force is applied through a die punch into the powder to cause compaction of the granulation. Compaction pressure is then defined as the applied force divided by the surface contact area between the die punch and the powder. A larger punch size requires more applied force to attain the same compaction pressure, which effectively limits the size of tablets that can be produced. For this reason, larger tablets tend in general to be softer because of the lower applied pressure (larger surface area).

Compaction pressures in the confectionery industry are typically defined in tons, which is actually a misnomer. The unit “tons” is actually a mass unit, similar to pounds (1 ton = 2,000 lb) or grams. However, just as mass is sometimes used to define a force (as in pounds-force), ton-force (or 2,000 lb-force) is also used to define the force applied to the die punch in tableting. The actual pressure then depends on the contact area between the punch and powder. A more correct unit for applied pressure is the MPa (megaPascal), although the confectionery industry generally does not use these units, preferring the older "ton" of pressure. Regardless of the units, only when the punch size is defined is there a simple conversion from applied force to pressure (force per unit area).

With that understanding of the terminology for pressure and force, confectionery presses are typically operated in the range of 2–10 tons of pressure. Typical presses used for candy manufacturing have maximum over-ride pressures in the range of 3–6.5 tons for "B" machines (maximum tablet diameter of 7/16–5/8 in. or 1.11–1.59 cm) and 10 tons for "D" machines (maximum tablet diameter 1 1/16 in. or 2.7 cm). This is the pressure at which the over-ride spring or hydraulic system will release the punch pressure. Note that presses are not run at these pressures because damage can occur to the press. The over-ride is simply a safety device. Many operators mistakenly think this is the actual tableting pressure. More expensive computer controlled machines, typical of those used in the pharmaceutical industry, can measure actual tableting pressure and tablet release forces.

The actual pressure at the tip of a set of punches is a function of the area of the tip. That means that a quarter inch diameter (0.635 cm) punch running on a thickness setting for a half inch (1.27 cm) tip will exert six times the pressure that the half inch punch will exert. The ratio is calculated as the ratio of the square of the radius of the tips. The quarter inch punch would have to be run at an over-ride of one-sixth of the half inch setting to provide the protection to the press and the tooling.

7.3.2.4 Safety in Manufacturing

Besides the safety and sanitation concerns of any food processing facility, tableting plants have additional concerns related to fine powders in the environment. Given the proper environmental conditions, the dust generated in operations of a tablet facility can ignite, leading to an explosion and subsequent fire. Dry conditions, abundant fine powdered particles and a spark are what it takes to have a powder explosion. Although relatively rare, when such explosions do occur, there is often significant structural damage.

Most facilities that are especially prone to powder explosions have various safety procedures and mechanisms incorporated into the plant operation. Such strategies include adequate cleaning procedures, proper construction design, and explosion containment devices. Most importantly, good housekeeping practices help to minimize dust build-up. Constant cleaning to minimize dust build-up will remove the potential for a dust explosion. Construction practices are also often part of the prevention process. Construction designs that minimize dust build-up help because they prevent accumulation of sufficient dust to foster an explosion. For example, minimizing pipe and ductwork near the ceiling of a plant and enclosing open construction materials (e.g., I-beams) help prevent dust build-up.

One element needed for a powder explosion is a confined space. Thus, plants with high powder explosion risk may be designed with, for example, a blow-out roof. That is, as soon as an explosion occurs and the pressure builds, the roof of the facility blows out, allowing the blast to release itself. This minimizes damage within the plant itself (but of course raises the roof). Fire containment strategies are also used to control fire explosions. These may be designed, for example, to release a chemical retardant at a strategic location if a pressure sensor indicates the onset of an explosion.

Through a combination of good manufacturing practices and proper facility design, the danger of powder explosions can be considerably reduced.

7.4 Product Characteristics

Tablets and lozenges are somewhat unique among confections since they are not made by boiling a sugar syrup to specific water contents. Instead, they are prepared by mixing powdered sweeteners with binders, either wet or dry. In the case of tablets, the powders are compressed under high pressures to force interparticulate bonding. The nature of the interparticulate forces determines the properties of the candy tablet. With lozenges, a combination of particulate bridging due to recrystallization (as the binder is dried) and adhesive action of the remaining liquid binder holds particles together and imparts the physical properties of the lozenge candy. Both tablets and lozenges are typically very hard, although hardness can be moderated to some extent through an understanding of the effects of formulation process conditions on the microstructure.

7.4.1 Microstructure

The arrangement of particles is slightly different between tablets and lozenges based on the different process for their manufacture and the forces that hold the piece together. In fact, lozenge formation is generally the starting point for tablet formation through wet granulation. That is, the dough made during wet granulation is either formed and dried to make lozenges or it is dried, ground and sieved to make a powder suitable to feed into the tablet press.

7.4.1.1 Lozenges and Wafers

A typical lozenge binder contains corn syrup, stabilizer (e.g., gelatin and/or gum arabic) and water, with a dissolved solids content around 40%. When this liquid binder is added to the powder base, a small amount of the base crystals dissolve in the water until the liquid phase equilibrates with the solid crystalline phase. Although the binder initially does not have any dissolved base material (sucrose, dextrose, sorbitol, etc.), once it has begun to mix with the dry powder, the base dissolves until the equilibrium solubility concentration for that particular mixture (see Section 2.8) is reached. Because the amount of binder added is relatively small and the crystalline content is still very high (>90–95%) in the mixture, a dough-like paste is formed. With the proper ratio of binder to base, this dough can be easily formed and shaped into the desired pieces.

The consistency of the dough depends primarily on the water content, although the amount and composition of the binder added have an effect as well. High water content gives a dough that is soft and pliable, but that may be prone to stickiness. If the water content (binder level) in the dough is relatively low, the dough is firm and may be difficult to form.

Upon drying to about 1–2% moisture, most of the water in the binder is removed, resulting in subsequent recrystallization of the sugar as the water is removed and a supersaturation is generated. Because the base particles are in such close proximity, it is likely that solid bridges form to hold some of the base particles together. Other particles are held together by the action of the hydrocolloid and corn syrup in the binder through capillary forces.

The water content of the dough has a significant effect on the hardness of the final product. A high water content in the dough means that a relatively large amount of liquid binder solution has been added to the powdered base. Thus, more base crystals dissolve in the water of the binder, meaning that more base must recrystallize when the lozenge is dried to the final water content (1–2%). More bridges are formed between the sugar particles and these structural elements lead to a harder product, one that requires more force to break. In contrast, dough made with low water content (relatively low binder addition level) means less recrystallized sugar, which generally leads to a softer wafer.

A combination of solid bridges, capillary forces, and hydrogen bonding forces are at work to hold the particles together in the dried lozenge. Depending on the relative extent of these forces, lozenge and wafer candies can be found with a wide range of hardness. In general, these candies are quite hard, such that they are either sucked in the mouth or crunched by the teeth with considerable force.

7.4.1.2 Compressed Tablets

During compaction under an applied pressure, a powder transforms from a free flowing mixture of independent particles to a unified tablet held together by various forces. The forces that hold the particles together in a tablet may be chemical (molecular) interactions between the particles or physical forces that prevent movement. Usually, a combination of physical and chemical forces holds a tablet together. The microstructure of a compressed tablet depends on the applied pressure, the dwell time under pressure, and the nature of the bonding forces between particles.

To make a tablet, a free-flowing powder of discrete particles (either individual particles or agglomerated granules) enters the die press where it is compressed at high pressures between two die punches. The initial stages of applied pressure cause rearrangement and, in some cases, fragmentation of the powder particles as the forces applied to any single particle increase. Rearrangement and fragmentation depend on the particle size and shape as well as the fracturability of the individual particles. Under applied pressure, the particles may also deform, either in elastic deformation or plastic deformation. Plastic deformation causes an irreversible change in shape, whereas elastic deformation means the particle returns, at least for the most part, to its original shape. Of course, these deformations result in further rearrangement under the applied pressure. At the same time, interparticle bonds are being formed as influenced by both electrostatic forces and molecular interactions (van der Waal's forces, electrostatic interactions, etc.). Furthermore, if any water at all is involved (for example in water of hydration in a crystal or even residual water in the granulation) there may be capillary forces that influence interparticle bonding. Any type of flow, whether due to the presence of water or deformation (plastic or elastic) of the particles can lead to formation of solid bridges between the particles when the pressure is released. These solid bridges result in formation of a strong, not easily broken, interaction between particles, which leads to a hard tablet. It is the sum of all the forces holding particles together that leads to the physical characteristics (density, hardness, etc.) of the finished candy tablet.

The combination of mechanisms holding any specific tablet together depends, to a large extent, on the type of granulation used to prepare the powder for compaction. In tablet formation following wet granulation, the binding between the aggregates of the granulation will certainly involve capillary forces. In wet granulation, the surfaces of the individual particles of the base (and other materials) are wetted by the binder (and other liquid ingredients). When this wetted powder is compacted and dried, capillary forces are responsible for holding the individual particles together in a granule. Although some aggregates are broken down by subsequent milling, many retain their aggregated nature when they are put into the tablet press. Application of force in the press causes rearrangement and fragmentation of these aggregates in the granulation, resulting in the physical forces holding the aggregates together. In this sense, the binder serves to hold the aggregates within the granulation together (often called binding), but it is primarily the physical forces exerted during compaction that hold the tablet together (often called bonding). Figure 7.7 schematically shows the granular and particulate structure of a tablet pressed from a wet granulation preparation. The two levels of structure, within the granules and within the tablet, are clearly evident.

In dry granulation, particularly in the absence of a significant amount of water, rearrangement and particle fragmentation are the primary mechanisms that lead to formation of a coherent tablet although particle deformation may also have an impact depending on the nature of the particles. A dry binder, like microcrystalline cellulose or maltodextrins, may be added to help

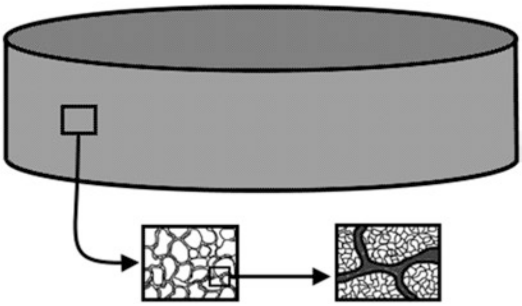


Figure 7.7 Schematic depiction of tablet microstructure when prepared from a wet granulation (After Alderborn and Wikberg 1996)

rearrangement and bonding of the crystals. However, because the dry binder is typically not as uniformly dispersed as the binder in the wet granulation process, more variability in the tableting process and in the final properties of the tablets may be noticed with dry granulation.

Direct compaction, similar to dry granulation, causes particulate rearrangement due simply to the applied forces. However, direct compaction does not work successfully for all tablet bases due to the nature of particulate breakdown. For example, although sucrose crystal powders have adequate flow properties and potentially can be directly compacted, tablets made by direct compaction of sucrose have tablet strength that is generally too low for confectionery products. Extensive fragmentation of sucrose crystals occurs under high applied pressures; however, it is thought that these fragments remain where they form instead of migrating into the interstitial spaces between larger particles to give stronger interparticle forces. Apparently, the large frictional forces between fragments prevent this migration and the result is weak tablets that break up too easily. Because of the poor compactibility of sucrose crystals, wet granulations were developed to make it more efficient for compaction. Dry granulations where sucrose crystals are blended with other materials (i.e., maltodextrins, polyols, etc.) to help compaction are now available.

7.4.2 Porosity and Density

Although it is probably hardness of candy tablets that signifies physical properties to the consumer, it is first necessary to understand the particulate nature of these candies and the powders from which they are made. Porosity and bulk density of a powder are functions of the size, shape, and interparticle forces between individual particles. A powder can be considered a mixture of a solid material (the particles with high specific density) and air (with low density). The amount of air entrapped between the particles of a powder determines the bulk density of the mixture and also the porosity, or the space between particles. The ability for molecules to move within the powder is primarily governed by porosity since it is only in this phase that molecules like flavors can move. Particle shape and size distribution are important factors in porosity. Uniformly large particles cannot pack as tightly as a mixture of large and small particles, nor can irregularly shaped particles pack as tightly as spheres. Thus, both particle size and shape greatly impact bulk density of a powder.

When a granulated powder is compressed, the particles are forced closer together, the volume of the powder bed decreases, its bulk density increases as more air is excluded, and thus, its porosity decreases. The void spaces between the particles or aggregates decrease as compaction occurs. The extent of compression, which is related to the applied force, determines the extent of decrease in volume and porosity, and consequent increase in bulk density. Bulk density can be defined as the apparent density of the powder or compaction and is given by the weight per bulk volume of the powder. Measuring bulk density requires accurate measurement of the height and diameter of the tablet (or powder column for the granulation prior to compaction). The relationship between particle density (ρ_s), bulk density (ρ_b), and porosity (ε) is given as:

$$\rho_b = \rho_s\left(1-\varepsilon\right) \tag{7.3}$$

According to Equation 7.3, as the void fraction of air in the tablet decreases with compaction, the bulk density of the tablet increases. Equation 7.3 can be rewritten for porosity:

$$\varepsilon = 1-\frac{\rho_b}{\rho_s} \tag{7.4}$$

Thus, porosity decreases as the bulk density of the tablet increases. As bulk density approaches particle density, the amount of entrapped air decreases and porosity decreases. This is exactly what happens during tableting, where a powder with high porosity is compressed into a tablet with higher bulk density (more particles are packed into the same volume). Porosity decreases during tableting, depending on the applied forces in the press and the nature of the granulation.

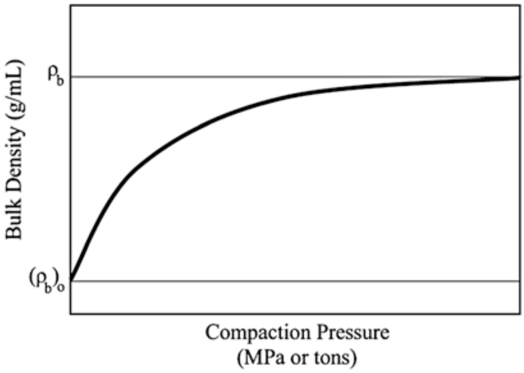


Figure 7.8 Typical increase in bulk density, ρ_b, with compaction pressure (After Shinohara 1984)

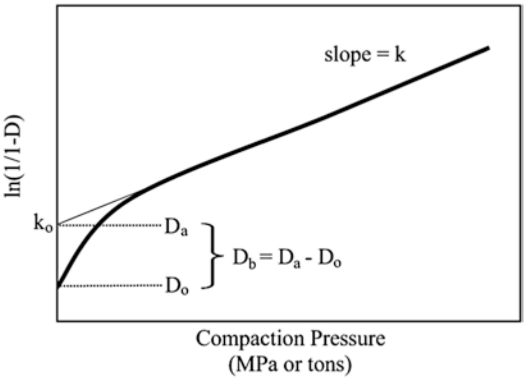


Figure 7.9 Typical Heckel plot showing change in relative density (D) with compaction pressure (After Paronen and Ilkka 1996)

In general, higher compression forces lead to thinner tablets with higher bulk density and lower porosity, although there is typically some upper limit where no further changes are observed with greater applied pressures. That is, particle fragmentation and flow reach some upper limit, beyond which no further rearrangements of individual particles are possible even with higher compression forces. The general trend of bulk density increasing with applied pressure during compaction is shown in Figure 7.8. At relatively low applied pressures is where the most significant changes in bulk density occur. At higher applied pressures, subsequent changes in bulk density are smaller since further changes in the particle distribution and orientation are limited.

The change in porosity, or volume, as a function of compression force describes the processes (and mechanisms) of powder compaction. Various models have been used to characterize these changes, with the parameters giving useful information on the general mechanisms of compaction. One of the most common compression models used in the pharmaceutical field is the Heckel model (Paronen and Ilkka 1996), given as:

$$\ln\left[\frac{1}{1-D}\right] = k_1 P + k_o \tag{7.5}$$

where D is the relative density (ρ_b/ρ_s), P is the applied pressure during compaction, and k_o and k_1 are empirical constants. The nature of the relationship between the inverse of the porosity (1-D) and applied pressure gives some indication of the mechanisms at work during compaction. Figure 7.9 shows a schematic Heckel plot, with the y-axis representing the Heckel parameter and the x-axis indicating compaction pressure. As compaction pressure increases, the Heckel parameter increases, eventually reaching a plateau at higher compaction pressures. The linear portion of the curve indicates where the Heckel model (Equation 7.5) appropriately fits compaction data.

The inverse slope of the Heckel plot, $1/k_1$, is often quoted to represent a mean yield pressure, which can be physically related to the mechanisms of compaction. Materials with a high value of the mean yield pressure (low values of k_1) are typically materials that are easily fragmented. Materials with a low value of mean yield pressure (high values of k_1) compact through either plastic or elastic deformation.

The parameter, k_o, represents the value of the Heckel parameter if the linear portion of the curve is extrapolated to zero compaction pressure. It is associated with an apparent initial relative density, D_a, of the granulation. The difference between D_a and the true initial relative density of the granulation, D_o, is a measure of how much rearrangement of the granulation occurs during the initial stages of compaction.

Numerous parameters can affect the response of a powder to compaction under pressure. Figure 7.10 shows typical Heckel plots for

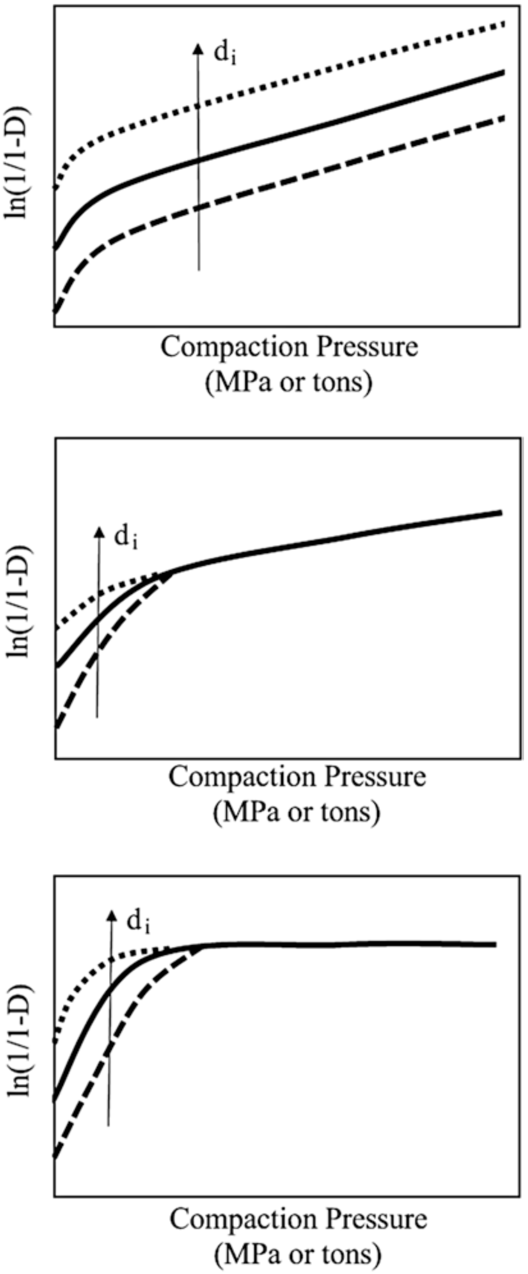


Figure 7.10 Heckel plots (D is relative density) showing different responses for initial particle size, d_i, based on prevalent mechanism of compaction. (**a**) Compaction attributed to particle rearrangement followed by plastic flow. (**b**) Compaction attributed to particle fragmentation. (**c**) Compaction attributed to plastic flow (no fragmentation) (After Paronen and Ilkka 1996)

different particle size fractions according to the dominant mechanism of compaction. In Figure 7.10a, the different particle size fractions started with different bulk density and retained that difference at all compression pressures. This behavior is attributed to compaction first by particle rearrangement followed by plastic flow. This behavior might be observed for amorphous materials that are easily broken and that exhibit plastic flow. In Figure 7.10b, the different particle size fractions again start out with different bulk density, but quickly come together in the same curve with applied pressure. In this case, compaction occurs due primarily to particle fragmentation. Once the particles are broken into fragments, they pack in the same manner regardless of their starting size. Sucrose granulations typically fit in this category. Finally, in Figure 7.10c, the material exhibits a sharp initial increase in bulk density followed by a leveling off where very little additional compaction occurs despite increasing pressure. In this case, different initial particle sizes do not result in different bulk densities in the plateau region. This is attributed to compaction by plastic flow with no particle fragmentation.

7.4.3 Mechanical Properties

These changes in structural attributes during compression lead to concomitant changes in the mechanical properties of the tablet. Of the mechanical properties of tablets, hardness is probably the most important in confectionery tablets since it correlates directly to a sensory attribute – the ability to break the confection in the teeth. Furthermore, an inverse relationship between hardness and dissolution rate typically applies for compressed tablets. That is, tablets made under higher compressive pressure are harder and will be more likely to dissolve slower, releasing flavors at a slower rate.

However, hardness is not an easily measured property. Numerous methods have been developed to characterize the physical attributes relating to how easily a tablet can be crushed. The best measurement method of hardness of a confectionery tablet would be one that simulated the action of breakage in the mouth. However, such simulatory methods tend to be qualitative in nature and do not provide information on the fundamental properties of the materials. Furthermore, it is generally impossible to ascertain anything about fracture mechanisms using these simulatory tests. Yet, the tests of fundamental mechanical properties do not necessarily correlate with sensory perceptions during consumption. This problem is typical of most rheological or mechanical property measurements in the food industry, not just the candy industry. Specifically, is it better to measure empirical parameters that correlate reasonably well with sensory properties or is it better to measure fundamental properties that give mechanistic information about the material but do not correlate very well with sensory measurements? Both types of measurements are probably necessary to allow a complete understanding of quality of food products.

The simplest tests for hardness involve application of a compressive force to the tablet. Either the force required to fracture the tablet can be measured or a penetration depth for a given applied compressive force can be used to characterize hardness. These methods give different values since they measure slightly different aspects of the tablet strength. A more fundamental measurement would be to correlate compressive stress (applied force over a unit area) to the measured strain in the tablet. The ratio of applied stress to measured strain (deformation) is a measure of Young's modulus of the material. A Young's modulus measured in this manner is dependent on the porosity of the tablet and is often extrapolated to zero porosity for comparison purposes.

Another method of tablet characterization is the diametral compression test, where two cone probes (point source) apply a force on opposite sides of the tablet. Fracture stress is usually obtained from this technique. Although this test does not exactly mimic consumers pressing a tablet between their teeth, it is often considered a decent simulation of hardness correlated with sensory measurements.

The strength of a tablet is influenced by many factors, including compaction pressure and particle size, as shown schematically in Figure 7.11. In both cases, for sucrose and lactose, an increase in compaction pressure gives an increase in tablet strength (e.g., hardness or force to fracture). However, in the case of sucrose, no effect of initial particle size was observed, whereas with lactose, tablet strength was higher when initial particle size was smaller. The difference in particle size effects between lactose and sucrose may be related to the mechanisms of compaction, due to the extent of particle fragmentation (number of interparticle binding sites), the binding force of interparticle bonds or some other mechanism. Sucrose is known to undergo significant (complete) particle fragmentation and, as a result, the hardness of sucrose tablets should be independent of particle size (Bolhuis and Chowhain 1996).

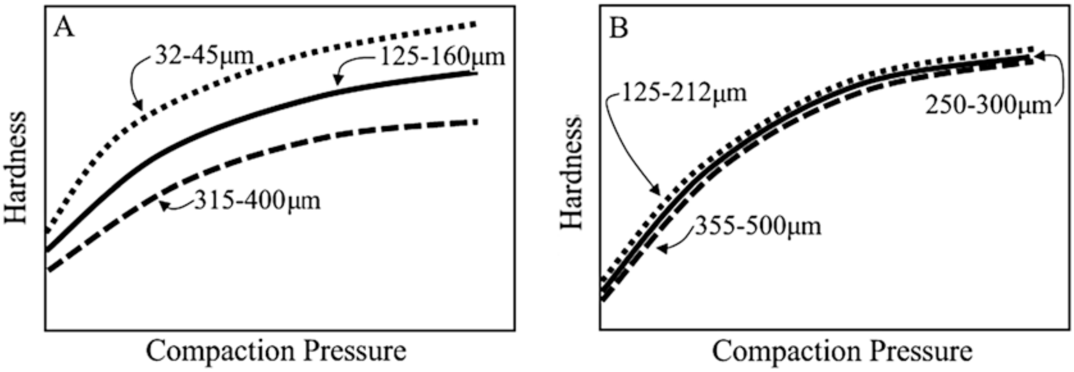


Figure 7.11 Increase in tablet strength with increased compaction pressure and different particle size: (**a**) α lactose monohydrate crystals; (**b**) sucrose crystals (After Alderborn and Wikberg 1996)

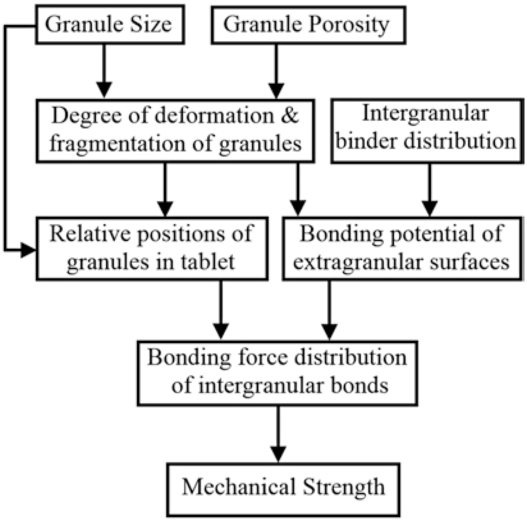


Figure 7.12 Summary of physical and chemical interactions among granules that influence tablet hardness (After Alderborn and Wikberg 1996)

In general, particle size must be within a certain range to produce high-quality tablet candies. The ideal size distribution for granules is 100% through a 20 mesh (841 μm) screen and 100% on a 60 mesh (250 μm). A particle size with 25% on a 100 mesh (149 μm) or 5% on a 325 mesh (44 μm) would be approximate limits. However, almost any size distribution can be handled with a good press.

In summary, Figure 7.12 shows schematically how attributes of the individual granules that make up a tablet influence the mechanical strength of the compacted product. Granule size and porosity, and distribution of the binder affect both physical and chemical bonding forces that hold the tablet together. The magnitude of these binding forces determines the hardness of the product.

7.4.4 Stability

The shelf life of tableted and lozenge candy is generally quite long, in large part due to the nature of the candy itself. Since these candies contain very little water and are primarily crystalline in nature, there are few changes that can occur over time during storage.

Sugar-based tablets and lozenges are resistant to moisture uptake from the air. As long as they are not exposed to water (which can dissolve them), these candies are very stable to moisture-related problems. Sugar-free tablets may be more hygroscopic and absorb moisture from humid air.

Notwithstanding potential moisture sorption issues, the main problems that occur during storage of tableted candies are either rancidity from the lubricant or oxidation of flavors. Proper selection of lubricant and flavors can slow or eliminate rancidity and flavor oxidation so that lozenges and candy tablets can last on the shelf for over a year with little to no change in quality.

7.5 Problems and Trouble Shooting

As with most confections, careful attention to the steps of ingredient preparation and product manufacture result in high-quality, consistent product. However, at times, unacceptable product may be produced due to problems caused either by improper ingredient preparation or problems in the tablet press itself. As a general rule of thumb, if the problem is consistent and repeatable, the tablet press operation is usually the cause of the problem. If the problem is more sporadic or inconsistent, however, the powder preparation or granulation is most likely the place to look. Some specific problems associated with tablet candies include pitting, capping, scoring, and variable tablet properties (thickness, weight, hardness, etc.). Improper environmental conditions (temperature and RH) in the mixing and process areas will also cause problems.

7.5.1 Pitting

Pitting, or sticking, occurs when the tablet sticks to the punch face, usually the upper punch, during tableting. There are several potential causes of this problem, including (1) wet or improperly mixed granulation fed into the tablet press, (2) worn or scratched punch faces, (3) failure of the lubricant to function as an anti-adhesive, or (4) a punch design that is too intricate for the granulation. The granulation tends to stick to designs with too many fine lines and intricate designs, which leads to pitting or sticking. This can be resolved by using a bit more lubricant. If there are wet spots within the powder granulation, the problem can come and go.

7.5.2 Capping

The problem of capping, or laminating, occurs when the tablet splits after it exits the press. Capping may be caused by air entrapment within the granulation, which results in separation of product layers upon ejection from the press. The solution to this problem is primarily with the granulation density. A higher density granulation means there is less air trapped between the particles and less chance of capping. If this is the case, adding some fines to the granulation may resolve the problem. Alternatively, capping may be caused by compression pressures that are too high, which results in loss of bonding by crushing the granulation and splitting upon release from the press. The solution is to reduce the applied pressure until the capping stops.

7.5.3 Scoring

If the lubricant is not functioning properly, there will be scoring on the belly band, or side, of the tablet, accompanied by noise and strain on the press. This problem may be caused by too low a level of lubricant in the formulation or improper addition of the lubricant (order of addition of ingredients is important in tablet making). The lubricant must be added as the last ingredient to ensure complete coating of the base particles and prevent problems during compression. The problem can also be caused by the presence of excessive fines. Alternatively, worn dies give a similar problem of scoring and noisy operation; however, the difference is that a worn die gives a uniform scoring of the tablet whereas problems with the lubricant give random scoring.

7.5.4 Variations in Size or Shape

Variations in tablet properties (hardness or size/shape) may occur due to problems in the press unit or to inconsistency in the granulation fed to the press. Variations in thickness of the tablet may be caused by variations in the length of the upper punch (consistent weight but variable thickness), a variation in the length of the lower punch (thicker tablets weigh more than thinner tablets), or variability in the bulk density of the feed granulation (random variations). Random variations in weight of the individual tablets may be caused by variability in the bulk density of the feed granulation or a problem with the feed frame of the press. Random variations in hardness of the tablets are due either to wearing on the upper compression roller or in the roller bearing itself. Variability in bulk density can also cause this problem.

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Hard Candy

8

8.1 Introduction

Hard candy covers a wide range of confections, although use of the term "hard candy" is confusing and not completely descriptive, with no agreement internationally about what candies fit into this category. Hard candies in the United States are typically (but not exclusively) sugar glasses formed by boiling to very high temperatures (low water content). In some parts of the world, hard candy sugar glasses are called "high-boiled" sweets in recognition of the temperature, the hard-crack state (see Section 3.2.1), to which they are cooked. However, there are candies that are cooked to the hard-crack state that are not sugar glasses; grained mints, for example, are cooked to high temperature, but are structurally more similar to a fondant with very high crystal content and low water content than they are to hard candy. Some compressed tablet candies are called hard candy because they are hard, even though they are not made by boiling sugar syrup to high temperatures to form a sugar glass. In contrast, other candies that are hard, such as crystalline candies like jawbreakers and rock candy, also typically do not fit into the "hard candy" category, primarily because they are not high-boiled sugar glasses.

Hard candy, as the term is used here, may be defined as a concentrated carbohydrate solution in which the majority of the water has been removed (final moisture content around 1–3%) and that has been cooled below its glass transition temperature (T_g) (see Section 2.10) quickly enough that sugar crystallization cannot occur (Hartel 2012). Thus, hard candy is an amorphous glass, of a similar molecular nature as window glass, although hard candy is made from sugar and window glass from silica. In fact, both sugar glass and window glass are just extremely viscous liquids that exhibit solid-like properties because of the extremely high viscosity. Their solid-like characteristic, which means they do not flow over an extended period of time, arises because they are held at temperatures below their T_g.

Hard candies come in a wide variety of shapes, sizes and characteristics. Besides the variety of flavors available, differences in hard candies arise from either the ingredients that are used (formulation) or the processing steps used to shape and form the product. Hard candy is often sold as drops, lozenges, barrels, rods, and sticks. For holidays, hard candy comes in the form of ribbons and disks of cut rock, with colorful and unique shapes worked into the interior of each piece. Hard candy may be aerated to change the appearance and texture, as found in candy canes and starlight mints. Lollipops of all shapes and sizes are sugar glasses that fit into the hard candy category. Hard candy may have other ingredients dispersed throughout the sugar glass matrix. Cough drops, for example, are hard candies with

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a functional ingredient (e.g., menthol) contained within. Carbonated candy (e.g., Pop-Rocks® and Carbonated Crystals®) is hard candy with pressurized carbon dioxide bubbles dispersed within the sugar glass matrix. Milk ingredients may be found in hard candy, for example in cream-based hard candy (Cream Savers®). As a cross-over candy from the caramel category, caramel hard candies are cooked to high enough temperature to create a sugar glass containing milk ingredients with color and flavor based on the products of the browning reactions (caramelization and Maillard browning).

Today, hard candies are primarily made from glucose syrup and sucrose, although a wide range of additional ingredients may be added to provide distinctly different characteristics (i.e., flavor, texture, appearance, etc.). The glucose syrup content may vary from a low of 10–15% to a high exceeding 60% (on a dry basis). The physical properties of the candy depend significantly on the nature of the glucose syrup and its percent content, as well as on the degree of inversion during cooking and, of course, on the final water content. Glucose syrup acts as a doctoring agent to retard sucrose crystallization, which allows hard candies to be made in large-scale continuous operations where otherwise sucrose would be likely to crystallize. Other ingredients used to add value or enhance consumer appeal include organic acids, colors and flavors, fruit juices, fats and cream. Sugar-free hard candies are made with sugar alcohols (i.e., maltitol, isomalt, etc.) and/or bulking agents (e.g., polydextrose) and may contain high-intensity sweeteners.

Although hard candies are found in a wide variety of forms and shapes, they are all made in essentially the same way. To make hard candies, the sugar syrup is boiled to remove water until the temperature reaches the "hard crack" (146–154 °C; 295–310 °F) state, as seen on candy thermometers (see Section 3.2.1). At these temperatures, water content is low (1–3%) and the viscosity of the sugar syrup quite high. When syrup at this temperature is dropped into cool water, it immediately solidifies into a hard brittle glass. Without vacuum cooking, temperatures exceeding 146 °C (295 °F) must be used. Vacuum cooking gives the desired water content at reduced temperatures (Section 2.7), which can retain desirable properties in the cooked candy mass (less color formation and sucrose inversion). Volatile, sensitive or reactive components, including colors, flavors and acids, are added after cooking to minimize sucrose inversion or flavor degradation and loss. The cooked candy mass may either be directly deposited into a mold to cool to the finished shape or it may be cooled to an intermediate temperature where it attains a plastic state. In this condition, the plastic candy mass can be easily manipulated to form the desired shape. If viscosity is appropriately high, the candy piece retains the desired shape for a long enough time that it can be further cooled to room temperature where it solidifies into a glassy material.

In some respects, the process of glass-blowing has many similarities to making hard candy. In fact, artisan chefs who make spun-sugar desserts are using essentially the same process as the glass-blower. To melt window glass (silica based), it is heated to a temperature where the viscosity decreases to the extent that the material flows sufficiently so that it can be formed into the desired shape. Once formed, the glass is cooled quickly to solidify the mass into the desired form. Whether silica, sugar or even polyols, the processes of making a glass are essentially the same.

However, unlike silica (window) glass, sugar glasses are not stable, being prone to moisture uptake, flavor loss, and sucrose crystallization. Sugar glasses are metastable materials that retain their properties for extended times as long as they are not exposed to improper conditions. Specifically, hard candies retain their desired characteristics as long as they are maintained in the glassy state. For one, storage temperature must always be below T_g. If storage temperature exceeds T_g of the hard candy, the piece is no longer in the glassy state and is prone to degradation. Degradation mechanisms include loss of flavors, stickiness, graining (sugar crystallization), and cold flow. Hard candies can have a shelf life of several years as long as they are always stored below T_g and protected from humidity.

The glass transition temperature of a hard candy is determined both by the ingredients used in the formulation and the processing conditions. However, even if a hard candy with sufficiently high T_g is produced initially, it may still undergo changes that lead to a rapid end of shelf life. Specifically, sugar glasses are notoriously hygroscopic and readily pick up moisture from humid air. Sugar glasses have Type 1 sorption behavior (see Section 3.4), meaning they readily pick up moisture even at low relative humidity. Since T_g decreases substantially with slight increases in moisture content, hard candy must be protected from humid air as much as possible. This is why hard candy is often found in double-wrapped bags, where each individual piece is separately wrapped and sold in an over-wrap bag. The two layers provide added protection against loss of shelf life due to moisture sorption.

Furthermore, flavor losses from hard candies are exacerbated by storage above the T_g of the candy. Diffusion of small molecules through the glassy matrix is limited by the extremely low mobility of molecules in the glassy state. When temperature exceeds the T_g of the candy, however, the ability of molecules to move (diffusivity) increases exponentially, resulting in increasing flavor loss with increasing temperature above T_g. If the hard candy grains (sugar crystallizes) because T_g has been exceeded, the flavors are concentrated in the uncrystallized phase and diffusion occurs even more rapidly. Thus, both physical changes and flavor losses can limit shelf life of hard candy if allowed to exceed T_g.

8.2 Formulations and Ingredients

Typical formulations for hard candy are shown in Table 8.1. Hard candies are made with a combination of sucrose and glucose syrup, whereas sugar-free formulations are made with one or more sugar alcohols. Other ingredients include colors and flavors, with organic acids sometimes added to bring out fruit flavors or to enhance a sour experience. Sometimes fats are added to provide certain flavor characteristics, improve eating quality, and reduce stickiness or tooth compaction. Some hard candies can be made with dairy products or fruit juices.

Table 8.1 Typical compositions (in %) of finished hard candy

	High sucrose	Low sucrose	Sugar free
Sucrose	70–80	40–50	–
Glucose syrup solids	20–30	50–60	–
Sugar alcohol	–	–	70–97
HSH[a]	–	–	0–30
Acid	0–2	0–2	0–2
High intensity sweetener	–	–	0.2
Flavor[b]	0.2–0.3	0.15–0.25	0.1–0.2
Color[c]	0.2–0.5	0.2–0.5	0.2–0.5

[a] HSH – hydrogenated starch hydrolysate

[b] Flavor levels will vary depending on the activity of the flavor

[c] General range for FD&C colors; may be higher for colors exempt from certification

8.2.1 Sweeteners

The main ingredients used in sugar-based hard candies are sucrose and glucose syrup, with the ratio chosen based on the desired end product characteristics. Higher glucose syrup levels (50–60% of the sugar solids; dry basis) prevent sucrose crystallization (graining) during storage, but generally lead to greater stickiness and make candies that are less sweet. Glucose syrup also aids in machinability of the hard candy mass, making the candy less brittle and easier to work with. This depends to some extent on the type of glucose syrup since, for example, high maltose syrup gives a more brittle candy and reduces machinability. Cost is also a consideration. In the United States, due to government price supports, glucose syrup is less expensive than sucrose; however, this is generally reversed in the world market.

The type of glucose syrup used in hard candy varies by manufacturer, although 42 DE glucose syrup is most common. Use of a higher DE syrup would add too much low molecular weight sugars (e.g., glucose), leading to a candy with a lower T_g and a product that is more susceptible to stickiness. Invert sugar is generally also present in finished hard candy from hydrolysis of the sucrose at high temperatures during processing. Invert sugar is sometimes added at low levels to the initial formulation to enhance flavor release, control crystallization and increase sweetness. Under certain cooking conditions, glucose and fructose may go through a reversion reaction, where long-chain polymers are formed. These polymers can have significant effect on candy properties. Although commercial hard candies contain a wide range, it is often said that the final DE of the finished candy should be around 16–18% to ensure a good quality, stable hard candy. This number should include whatever reducing sugars are added through the formulation (glucose syrup, invert sugar, rework, etc.) as well as those produced during manufacture (for example, through inversion).

Sugar-free hard candies make up an ever-increasing segment of the category. The first sugar-free hard candies were made with sorbitol, although because of the low T_g of sorbitol, it was actually a crystallized candy and not in the glassy state. The availability of isomalt and maltitol, as well as hydrolyzed starch hydrolysates (HSH), has improved the quality and accessibility of sugar-free hard candies. For the most part, sugar-free hard candies are now made with isomalt, maltitol or HSH, or combinations thereof. Since sugar alcohols are typically not sufficiently sweet on their own, sugar-free hard candies require addition of a small amount of high-intensity sweetener to provide sufficient sweetness. Common high-intensity sweeteners for sugar-free hard candies include sucralose, acesulfame potassium (AceK), and aspartame (see Section 1.9).

8.2.2 Flavors

Flavors are added to enhance consumer appeal and satisfaction, although they often add a substantial cost to hard candy. Selection of flavor is based on the desired flavor characteristic in the final product, the stability of the flavor, and the necessary use level, in addition to the cost. Choice of flavor must be made in conjunction with choice of color to ensure satisfactory consumer perception. Flavors may come from natural or artificial sources, or a blend of both may be used. Salt may often be added at very low levels to enhance the flavor and reduce sweetness. Salt is particularly effective in enhancing the flavor profile of butter, butterscotch, caramel, and toffee flavors.

Typically, flavors are added after the cooked candy mass has cooled somewhat to minimize loss of volatile components and so that high-temperature reaction products that lead to off-flavors are not formed. However, temperatures are still likely to exceed 121 °C (250 °F) at the point of flavor addition and some changes in flavor and flavor loss are inevitable. Some estimates suggest that adding flavors under atmospheric conditions at the end of a cook results in up to half of the flavor being lost to volatilization. Furthermore, since different flavor components are likely to have different relative volatilities, some will be lost to a greater extent than others and the end flavor profile may be quite different from the intended flavor profile of what was added. Higher retention levels would be expected for direct in-line addition of flavors where volatile components cannot escape into the atmosphere. Large-scale continuous processing lines that incorporate flavor directly into the fluid sugar mass through in-line static mixers have significantly less flavor loss than atmospheric systems and thus, require lower flavor addition levels. Regardless of how flavors are added, they need to be completely mixed in the fluid sugar mass before depositing or “pooling” of the flavor can occur, resulting in inconsistent flavoring in the finished candy. In some instances, citrus oils may need to be diluted in alcohol to be completely mixed into the candy mass. As always, the effects of the flavor carrier, or solvent, on the properties of the sugar glass must be considered.

Since liquid flavors are added after the final water content has been reached, the flavors should be as concentrated as possible to minimize the amount of liquid added back to the hard candy mass. Depending on solvent, addition of liquid flavors can lower the glass transition temperature, making the candy more susceptible to changes (graining, stickiness, flavor loss, etc.) during storage. Often, oil or propylene glycol-based flavors are used in hard candy to minimize such problems, although these systems may affect other properties of the candy. Oil-soluble flavors are usually used in the case of citrus and mint nuances. Theses types of flavors are insoluble in propylene glycol, but can be diluted in ethyl alcohol, a clean oil or medium-chain triglycerides.

In addition to the conditions at which flavors are added (atmospheric versus enclosed), flavor addition levels depend somewhat on the flavor type and source. Most flavors, both natural and artificial, are added at a level of about 0.2–0.3%. However, some traditional natural flavors (e.g., juice concentrates) may be added at levels as high as 1–1.5%. The higher usage level of natural flavors is due to their limited concentration and activity. With all flavors, the shelf life of the flavor is extremely important.

Flavors potentially can undergo degradation during shelf life of hard candies. Besides gradual diffusion of flavors out of the candy matrix, there are potential reactions that can take place that alter the nature of the candy flavor. Citrus and mint flavors tend to oxidize quickly on their own. If these types of flavors are diluted in oil (soybean, sunflower, vegetable, corn, etc.), the oxidation factor increases due to the rate of oxidation of the oil and the storage conditions. Some flavors are pH sensitive, so that combinations with organic acids must be chosen carefully. Flavors may also react with colors. This reaction may occur with chocolate, caramel, and toffee flavor, among others. Furthermore, if the flavor contains an inherent dark tone due to the raw materials, it can make the final candy unacceptably dark.

8.2.3 Colors

Proper choice of color in hard candy is crucial since, along with flavor, it is one of the more important selling points. A vibrant color that matches the flavor is critical to establishing a high quality hard candy. Despite their importance to candy attributes, typical use levels of colors in hard candy are generally less than 0.2% depending on final color intensity desired and base color used. The usage rate for exempt colors are generally higher than FD & C dyes.

Choice of color is also important. Whether to use certified colors or colors exempt from certification depends on the application, the perceived benefits of one or the other, the actual color desired, the ease of use, cost, and ultimately, the regulatory limits established by the countries in which the candies are to be sold. The seven certified FD&C (based on the federal Food, Drug & Cosmetic Act) colors approved for hard candy use in the United States include Red #3, Red #40, Blue #1, Blue #2, Yellow #5, Yellow #6, and Green #3. Most of these colors can be found in either dye (individual molecules in solvent) or lake (dye molecules bound to a small aluminate particles) form. Note that Red #3 lake is no longer approved for use in the United States. Other colors that might be used include caramel color, beta carotene, turmeric, carmine, red beet juice, and titanium dioxide (not more than 1% as per 21CFR 73.575). The specific color that works best for a particular application depends on the intended effect. The FD&C certified colors are easy to use, are relatively inexpensive, are often use in smaller quantities, and are usually more stable and consistent than colors exempt from certification. On the other hand, naturally-derived colors have better acceptance from a labeling view point.

Colors in hard candies may be added as solutions, dispersions, pastes, color cubes, or color granules (see Section 6.1), depending on the application. As with flavors, addition of liquid colors after cooking should be limited to prevent undesirable physical changes. Color pastes or granules provide an efficient means of coloring hard candy without causing undesirable effects.

Changes in appearance and color may occur with certain types of processing. For example, aeration or pulling introduces small air pockets into the plastic sugar mass that change coloration. Aeration typically leads to whitening of untinted hard candy as the bubbles refract light.

Table 8.2 Stability of coloring agents in hard candy applications (Srnak, unpublished)

Color	Light	Acid	Heat
Blue #1	Good	Good	Good
Blue #2	Pathetic	Pathetic	Poor
Red #3	Poor	Pathetic	Good
Red #40	Very good	Good	Good
Yellow #5	Good	Good	Good
Yellow #6	Moderate	Good	Good
Turmeric	Poor	Good	Very good
Beta carotene	Good	Very good	Good
Annatto	Fair	Fair	Good
Carmine	Excellent	Good	Very good
Red beet juice	Fair	Fair	Poor

In colored hard candies, aeration causes softening of the colors into pastel-type shades. Some colors may change due to the high processing temperatures or the low pH found in some acidified candies.

Stability of colors in hard candy during storage can be a concern – especially exempt (natural) colors. Each colorant has a distinct response to environmental stresses (light, acid pH, heat, etc.). Table 8.2 provides stability guidelines to light, acid and heat for a variety of colors used in hard candies.

8.2.4 Organic Acids

Acidulants are often used to provide tartness, especially for fruit-flavored candies. Malic, citric, tartaric and lactic acids are often used, with citric acid being most common. Besides cost, functionality of the acid plays an important role in ingredient selection. For example, lactic acid may be used to enhance dairy flavors and/or in deposited hard candies where buffering and low moisture solutions are important. Also, certain acids match best with certain flavors (i.e., tartaric with grape, malic with apple, citric with lemon, etc.). Combinations of acids may be used to provide a specific intensity profile (maximum sensory intensity and duration of flavor release) for flavor and acid perception (see Section 6.3). For reasons of cost and simplicity, however, typically only a single acid is used as complement to a variety of flavors. Hard candies that cater to consumers who enjoy the sour experience may contain a dusting of powdered acid on the surface in addition to a pocket of powdered acid within the center of the candy piece.

Since acids cause inversion of sucrose, particularly at elevated temperatures, they are added after cooking, at the same time as the flavors. The production of glucose and fructose due to inversion of sucrose at low pH and high temperature leads to unstable candies, with lower T_g and greater hygroscopicity. Shelf life is greatly reduced. Buffering salts, such as sodium citrate, may be used to offset potential inversion problems when acids are added earlier in the process.

8.2.5 Fats

Fats may be found in certain hard candies. For example, butterscotch, buttermint and chocolate flavored hard candies may contain from 2% to 10% fat to provide the desired flavor and mouthfeel. Fat, which forms a fine emulsion/droplets in the aqueous sugar phase, decreases the hardness of the candy but increases brittleness. Fat also generally reduces moisture uptake and stickiness (to manufacturing equipment during processing and teeth during consumption).

Hard candies with high content of unsaturated fats may be prone to off-flavor generation due to lipid oxidation during storage. In these cases, flavor can be used to mask any off notes generated.

8.2.6 Fruit Juice

Fruit juices may be used in making hard candies; they are generally added as concentrates after the cook step. The intense thermal process for manufacturing hard candies generally means much of the desirable flavor aspects of the fruit juice would be lost in processing. Further, the organic acids in fruit juices would also be problematic during cooking (increased inversion). They also contain low molecular weight sugars that might decrease T_g and negatively affect shelf life. For these reasons, higher cook temperatures may be required for hard candies where fruit juices are added after cooking. Fruit juices also may be used for the center of filled hard candies.

8.2.7 Dairy Ingredients

Dairy ingredients are sometimes used to provide both flavor and textural attributes to hard candies. Hard caramels, a cross between the hard candy and caramel categories, make use of dairy ingredients for the desired color and flavor. Typically, concentrated dairy ingredients like sweetened condensed milk, cream or butter are added to the batch during cooking. The dairy ingredients (proteins and lactose) participate in the Maillard browning reaction (see Section 1.4.3) to produce unique flavors, which are difficult to reproduce artificially. Milk fat also provides desirable cooked butter flavor notes.

8.3 Processing

The general steps for manufacture of hard candy are shown in Figure 8.1. Although numerous variations of this process have been developed over the years, hard candy is still generally made by cooking sugar syrup to a temperature that yields the desired water content (the hard crack state), cooling a little prior to adding flavors and acids, cooling further to the plastic state, followed by forming. Alternatively, liquid candy can be deposited into molds and allowed to cool.

Processing of hard candy can be done either as a batch process or on a continuous production line. Many small candy makers still produce hard candy in small (even as small as 100 pound) batches. However, larger manufacturers now use fully automated and controlled processing systems for high-throughput (thousands of pounds an hour) of consistent high quality product.

Figure 8.2 documents the approximate steps for typical hard candy manufacture on a phase/state diagram (see Section 2.11 for more details). The specific location of the solubility and glass transition curves depends on the specific make-up of the hard candy formulation and the effects of processing on ingredients (e.g., inversion of sucrose to create invert sugar), with Figure 8.2 showing the conditions for a 70:30 (w/w) mixture of sucrose and glucose syrup solids. The initial sugar mixture is pre-heated to its boiling point, dependent on water content and composition. The initial starting point depends somewhat on whether the process is batch or continuous. The amount of water lost during heating is dependent on the rate of heating and atmospheric conditions. Typically, evaporation losses are minimal during the heating stage and it is not until boiling commences that significant water loss occurs. As the syrup continues to boil and water content decreases, the boiling temperature increases according to the boiling point elevation curve. Note that the boiling point elevation curve crosses the solubility curve as water is boiled off so that the syrup quickly becomes supersaturated even while boiling. The boiling point elevation curve

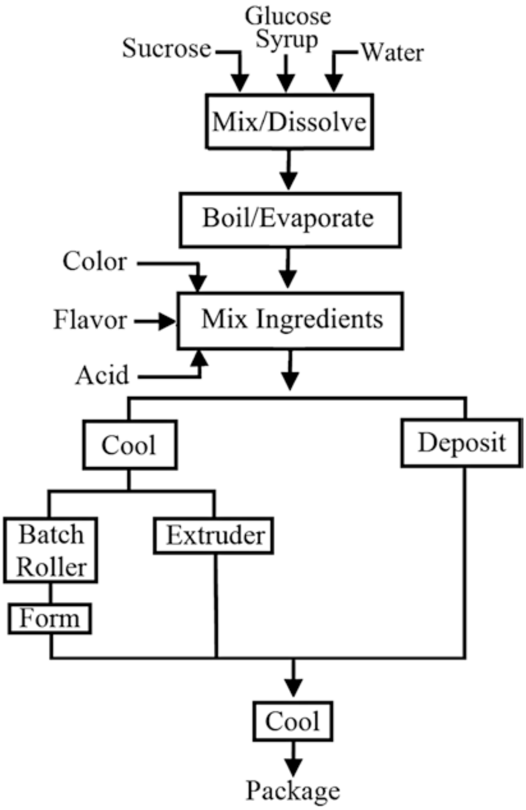

Figure 8.1 Typical process flow diagram for hard candy manufacture

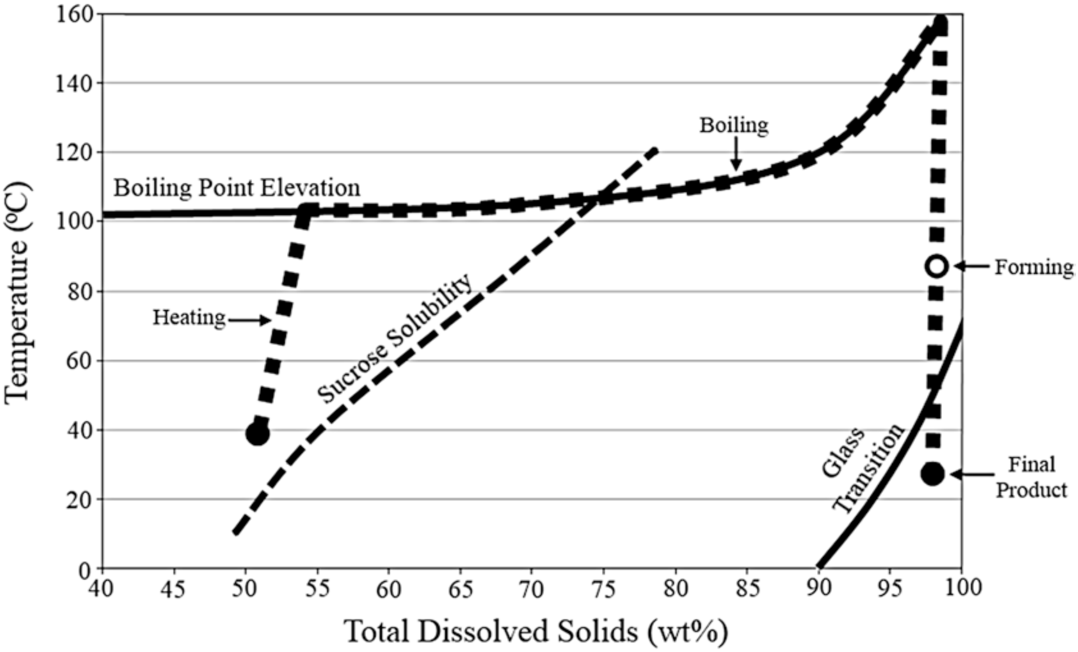

Figure 8.2 Progression of hard candy manufacture via plastic state formation on phase/state diagram. Lines representative of mixture of 70% sucrose and 30% 42 DE glucose syrup solids on a dry basis (With permission from Hartel et al. 2011)

is followed up to the temperature that corresponds to the desired final water content. At this point, the syrup is either deposited into molds while still hot or cooled to some intermediate temperature where the sugar mass attains a plastic state for forming. Sugar crystallization is possible at this stage since the mass is being held at warm temperatures, in the supersaturated state. Doctoring agents (glucose syrup, invert sugar, etc.) retard sugar crystallization sufficiently during this stage and, once the candy mass is cooled to room temperature, the loss of molecular mobility at the glass transition point limits crystallization so that the finished product is in the glassy state.

8.3.1 Typical Process Steps

Although processing steps may vary slightly depending on the scale of production, hard candy manufacture typically follows the general steps described below.

8.3.1.1 Mixing and Dissolving

The first step of hard candy manufacture generally involves mixing ingredients and dissolving sucrose. Traditionally, granulated sugar is used in conventional hard candy, but it must be fully dissolved in water to ensure there are no crystals remaining in the final glassy product. A sufficient quantity of water must be added and enough time given for the sugar to dissolve at warm temperatures to ensure that no crystals are carried through into the hard candy.

In small batch processing, the sugar, glucose syrup and extra water are added in the kettle (usually copper or stainless steel) and heat is applied. The heat source may be steam or direct gas flame. A gas flame on a copper kettle gives rapid and uniform heat transfer, and allows the operator adequate control of the process. The initial heating stages are where the granulated sugar dissolves in the added water. Although sufficient water is needed for dissolution, addition of too much water is also undesirable since it means boiling takes longer to reach the desired final moisture content. About one-third the weight of sucrose in the formulation is added as extra water, but this depends substantially on the amount of glucose syrup in the recipe. Typically, about 30–35% of the batch is water, whether from glucose syrup (which is about 19% moisture) or additional water added.

In larger-scale operations, continuous dissolvers are used to promote rapid dissolution of the sugar prior to cooking. Dissolvers are often coils in a steam chest or straight-through shell and tube heat exchangers through which the sugar mixture at low pressures is pumped to allow sufficient residence time as the temperature is increased. Less water, only about 15–20% of the batch, is needed in these continuous dissolvers, compared to open kettles.

To promote even more rapid dissolution of sugar in high-throughput operations, a pressure dissolver system may be used. Here, the elevated pressure enhances dissolution because the water remains liquid for a longer time. In open batch cooking, water begins to vaporize as soon as the boiling point is reached. If the granulated sugar has not dissolved by the time temperature reaches about 112 °C in an open kettle, any undissolved sugar will remain as crystals since the solubility line is crossed (Figure 8.2). In a pressure dissolver, the water remains in liquid form until the pressure is released, enhancing dissolution at elevated temperatures. Once dissolution is complete, liquid water is flashed off as the pressure is released back to atmospheric conditions. Often, a shell and tube heat exchanger is used to quickly heat the syrup under pressure to promote dissolution (see Figure 8.3). With some continuous pressure dissolvers, the water content of the sugar mass pumped into the cooker may be as low as 10%. As long as there is sufficient residence time at elevated temperatures and pressures, dissolution will still be complete.

In some very high-throughput hard candy manufacturing facilities, dissolution may be bypassed by using liquid sugar rather than granulated sucrose. Although the concentration of liquid sugar is about 67% (the solubility concentration at room temperature) and more water must be evaporated than in previous systems, the main advantages of using liquid sugar is that it can be pumped directly to mix with glucose syrup (also liquid) and then directly into the cooker. There is no longer a need for a dissolution step, giving a distinct reduction in processing time. Other advantages include control of ingredient dosing with simple flow meters and reduction of potential dust hazards inherent with sugar powders.

Figure 8.3 Pressure dissolver (Courtesy Hänsel Processing GmbH)

8.3.1.2 Cooking

Once the sugar has been dissolved, the sugar syrup is heated further to the point where it begins to boil. As water is removed with boiling, the temperature of the syrup increases according to the well-known relationship between boiling point and water content; thus, the temperature increase during cooking of sugar candy masses generally follows the boiling point elevation curve. Knowledge of the boiling point elevation curve for the sugar mixture in the formulation is required to control the water content of the final product. In fact, since it is nearly impossible to accurately measure solids content of hard candy masses at such elevated temperatures, water content of the final candy piece is generally governed by the temperature to which the sugar mass is cooked. The specific mixture of sugars (sucrose, glucose syrup, invert sugar, etc.) determines the boiling point elevation curve so that different cooking temperatures may be required to obtain the same water content for different formulations. Further discussion of formulation effects on boiling point elevation can be found in Section 2.7. Typically, cook temperatures of 146–154.5 °C (295–310 °F) are used to obtain water contents of 1–3%. On Figure 8.2, the trajectory during cooking follows along the boiling point elevation curve.

During cooking, certain reactions (see Section 8.4.1) can occur that may influence the final product characteristics. These reactions include color formation, inversion of sucrose and reversion of monosaccharides into polysaccharides, each of which occur at a faster rate at higher temperatures. Thus, a vacuum cooker is often used to attain the final concentration since, when heat is applied under vacuum, water boils at lower temperature than at atmospheric conditions (see Section 2.7). Consequently, the same water content can be attained at lower temperatures under vacuum, and negative reactions (i.e., color formation, inversion, etc.) can be minimized. In principle, a candy mass cooked under vacuum has less color (is less brown) and less inversion of sucrose than the same mass cooked at atmospheric pressure due to the lower cook temperature and shorter process times. Often hard candy batches are pre-cooked to about 130 °C (266 °F) at atmospheric pressure and then finished in a vacuum cooker operating at approximately 27–29 in Hg vacuum[1]. Under this vacuum, temperatures of only about 141 °C (286 °F) are needed to attain a water content of ≈2% (compared to 150–160 °C at atmospheric pressure).

Small batch cookers can handle approximately 45.4 kg (100 lb) of candy mass. To enhance production capacity, semi-continuous cookers were developed. These systems use multiple batch, vacuum kettles cooking syrup at staggered intervals to give nearly continuous output of cooked syrup. While one batch is being cooked to final moisture content under vacuum, another kettle is being filled. Once filling is complete, the next kettle is filled, and so on. When a kettle has completed cooking, the vacuum is broken and cooked candy poured out for further processing. These systems increase capacity of production substantially over a single batch cooker.

For large-scale production of hard candies, completely continuous dissolvers and cookers are often used to produce a continuous flow of cooked sugar syrup. Various types of continuous cookers are available. Some use microfilm (sometimes called thin film) cooking technology to rapidly remove water from the syrup. In a microfilm cooker, a thin layer of syrup flows across a surface that is sufficiently hot to induce rapid boiling and lower the water content of the sugar syrup within minutes. The heat transfer surface is continually swept by rotating blades to promote rapid cooking, with minimal sucrose inversion and color formation.

Alternatively, a shell-and-tube or a spiral tube (coil) heat exchanger can be used to provide rapid heating and cooking (in minutes). Rapid cooking results in minimal inversion and other degradation reactions; thus, the resulting syrup is clear. Vacuum operation is common to reduce boiling temperature and further reduce degradation reactions. Figure 8.4 shows a typical high-capacity cooking system. However, one distinct disadvantage of the continuous cooking systems is that the candy mass experiences more shear, particu-

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[1] Specification of a vacuum is based on an inverse pressure scale and is almost always given in units of inches of mercury (in Hg). That is, rather than increasing from absolute zero pressure, a vacuum scale increases numerically as pressure is reduced below atmospheric pressure. For example, since atmospheric pressure is 29.92 in Hg, a complete (absolute) vacuum would be 29.92 in Hg vacuum, equivalent to zero absolute pressure. A vacuum of 28 in Hg would then be the equivalent of an absolute pressure of 29.92–28 = 1.92 in Hg. Note: atmospheric pressure = 29.92 in Hg = 760 mm Hg = 101.325 kPa = 1.01325 bar = 14.696 psi (pounds per square inch).

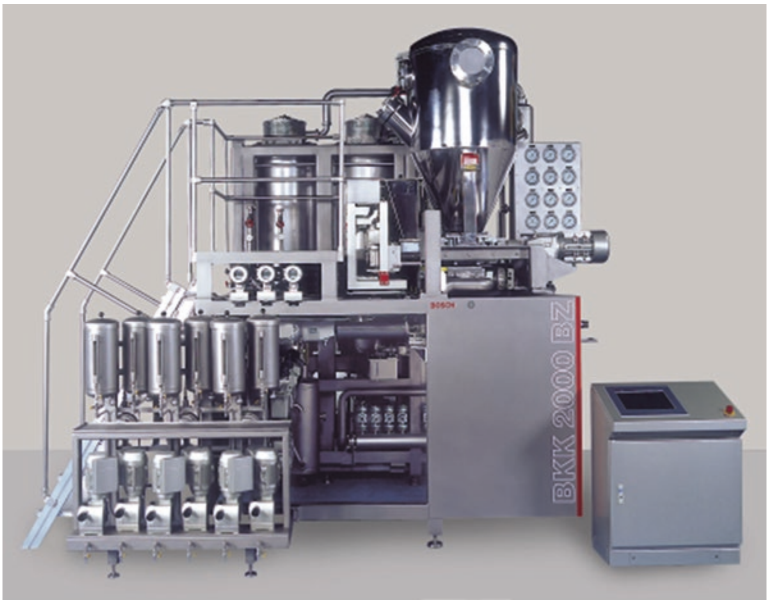

Figure 8.4 High-capacity cooker (Courtesy of Robert Bosch GmbH)

larly at the extraction pump where it is removed from the vacuum, compared to batch cookers. This shearing occurs at a point when the mass is most sensitive to graining, within the crystallization zone of the state diagram (see Figure 8.2). Since supersaturated sugar syrups are prone to crystallization under the shear forces in continuous cookers, slightly higher levels of glucose syrup (at least 30%) as a doctoring agent are generally needed to prevent graining.

8.3.1.3 Color, Flavor and Acid Addition

Once the candy mass has been cooked to the desired water content and cooled sufficiently, heat-sensitive ingredients are blended into the mass. Colors and flavors can undergo changes due to exposure to high heat, so are generally added after the cooking step, when the candy mass has cooled somewhat. If the flavors were added during the cooking stage, almost all of the volatile chemicals that make up the flavor would be lost during cooking since flavor molecules tend to be more volatile than water (they boil at a lower temperature).

Even addition of volatile flavors at temperatures of 121–138 °C (250–280 °F) can result in significant losses (sometimes estimated at upwards of 50%), particularly when they are added at atmospheric pressure. For this reason, metering pumps and dosing screws with self-contained in-line mixers (not vented to the atmosphere) are often used to minimize flavor loss in continuous systems. Once the colors and flavors are thoroughly mixed within the candy mass and the mass begins to cool toward the plastic state, flavor losses are reduced considerably. The high viscosity of the candy mass limits diffusion of the flavor molecules so they are retained within the sugar syrup. However, high viscosity also means it is more difficult to mix/blend liquid (or solid) ingredients within the candy mass. This means there is a compromise between hot addition of flavors (low viscosity to minimize pumping pressures) versus flavor degradation at elevated temperatures.

Organic acids are also added after cooking, in this case to control sucrose inversion due to the low pH. If the acid were added during the cook, the reduced pH environment would lead to excessive inversion. The resulting invert sugar (glucose and fructose) would lead to problems due to the decrease in T_g associated with these monosaccharides (see Section 2.9). The low molecular weight sugars (particularly fructose) would also lead to increased hygroscopicity and stickiness. Since the rate of inversion of sucrose depends on temperature and pH, addition of acids at the lowest temperature feasible after cooking is desired.

Acids may be added in powdered form or as a concentrated liquid. Often, acid is added as a fine granulation for adequate dispersion within the cooked mass. If a concentrated liquid acid is added, the extra water must be accommodated in the batch by boiling to slightly higher temperature.

8.3.1.4 Cooling

After cooking, the candy mass must be cooled rapidly to prevent sugar crystallization (Figure 8.2). Two distinctly different methods of cooling and forming are used in commercial hard candy production. In the more traditional method, the hot candy mass is cooled into a plastic state, the candy pieces are formed, and then the formed pieces are cooled further to set them into the glassy state at room temperature. Alternatively, the hot fluid candy mass can be poured into a depositor and filled into appropriate molds. Cooling of the molds allows solidification of the candy mass into the glassy state. Depositing of hard candies has evolved rapidly in recent years so that numerous multi-colored shapes and designs can be formed.

In small batch systems, a cold table may be used to cool the sugar syrup to reach the plastic state for forming. The cooked sugar mass at elevated temperature has a viscosity that allows it to flow readily. That is, when the candy mass is poured onto a table, it will flow quickly and rapidly fill whatever borders are used. Once the sugar mass cools a little, though, it becomes sufficiently viscous that it can be kept confined on a tabletop as it cools further. To ensure rapid cooling, the viscous candy mass is turned periodically, either by hand or with mechanical plows, to expose a different (warmer) surface to the cooling table. Typically, flavors, colors and acids are added at this point to minimize losses due to volatilization at higher temperatures. Folding the candy mass on the cold table serves to distribute the ingredients throughout the candy mass at the same time cooling takes place.

Alternatively, the hard candy mass can be cooled by forming into a thin sheet on a cooling drum. The hot candy mass is distributed onto the top of the drum and, as the drum slowly turns, the refrigerant contained within causes rapid cooling. By the time the candy mass reaches the bottom of the arc, it has cooled substantially and can be scraped off the drum into a hopper for further processing.

Another approach to cooling hard candy mass is on a cooling conveyor belt, with cooling water underneath the belt and plows that turn the mass to enhance cooling. A wide sheet of candy mass may be turned several times on the conveyor until the mass reaches the plastic state. Volatile flavors and granulated acid may be applied at the start of the cooling conveyor to be sufficiently worked into the mass by the time cooling is completed.

As the candy cools and solidifies, it becomes increasingly viscous until it reaches a somewhat plastic state. At this point, the candy shape can be formed. The candy mass at this point must have exactly the right consistency or the product will not form correctly. If the candy mass is too viscous (too cool), it will not form into the desired shapes and crack as it is formed. Yet, if it is not viscous enough (too warm), the mass still flows after the shape is made and the desired shape is not retained. Thus, control of temperature is critical at this point in the process. Typically, forming takes place at temperatures of 80–88 °C (175–190 °F).

From Figure 8.2, at forming temperatures (indicated by the circle as the mass is cooled), the candy mass is in the crystallization zone for sucrose, which makes the candy mass prone to graining at this point. Fortunately, the high viscosity and the inhibitory effects of glucose syrup, slow the rate of crystal nucleation sufficiently so there is a period of time during which the candy can be formed without significant risk of sugar crystallization. If the candy mass is held for too long at this temperature or worked too vigorously, graining eventually occurs. Eventually, even a 50:50 mixture of sucrose and glucose syrup will crystallize if held long enough at a temperature above its T_g.

In fact, in some commercial hard candies, sporadic crystallization may occur during forming such that a few sugar crystals are present in the candy mass. If a candy mass containing a few crystals is cooled quickly to a temperature below T_g, those crystals remain imbedded within the glassy matrix and are relatively stable (as long as storage conditions are favorable). That is, as long as the candy remains in the glassy state, these crystals are not a real problem since mobility of sugar molecules is so low in the glassy state that these crystals do not grow despite the extremely high supersaturation. However, crystals embedded in the hard candy can cause problems during storage, especially when the temperature exceeds the glass transition temperature of the candy (see Section 8.4.3.2).

8.3.1.5 Forming

Numerous methods have been used for forming hard candies, whether through formation of a plastic rope of candy or through direct depositing of hot, molten candy mass. Over the years, the traditional methods of hand cutting and forming of hard candy have been replaced by more efficient continuous forming methods that allow very rapid and high-capacity production of consistently high-quality hard candies.

The traditional method for forming hard candies involves forming the plastic candy mass into a rope that can be cut into the desired shape. Batch rollers and sizing rollers are still in common use for forming candy ropes, although the use of extruders for producing a continuous rope of candy mass for forming is becoming more common.

Batch rollers are devices that have horizontally rotating conical tapers, often with ribs to prevent sticking, promote cooling and provide traction between candy mass and rollers. The batch roller (Figure 8.5) uses a combination of gravity and rolling action to spin the large diameter candy mass into a smaller diameter continuous roll of candy for feeding the sizing rollers. By alternating direction of operation (to prevent a corkscrew formation of the candy), the conical rollers reduce the plastic candy mass diameter to about 2–5 cm (0.8–2 in.), depending on the desired size, ready for sizing and subsequent forming into the desired shapes.

In large-scale hard candy processes, extrusion forming is becoming more common due to the high production capacity, ease of use, and consistency of product. Candy extruders are primarily forming units, with no cooking of the mass within the extruder (contrary to cooking extruders often used for snack production, where significant cooking of the mass takes place within the extruder barrel). The candy mass is forced by the screw element against a die plate at the exit of the extruder to produce a rope of plastic sugar, ready

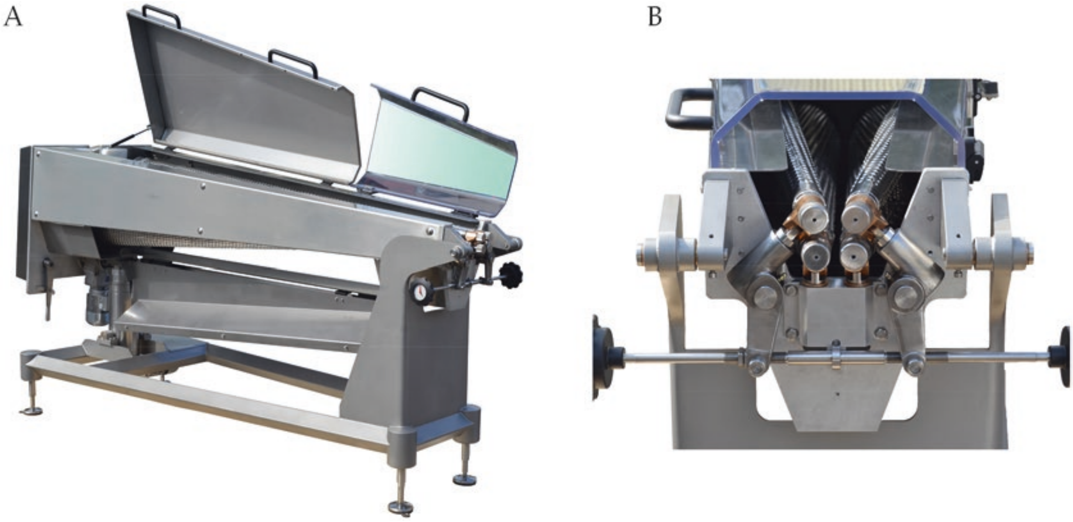

Figure 8.5 Batch roller for hard candy: (**a**) side view; (**b**) end view (Courtesy of AMP Rose)

for subsequent forming (Figure 8.6). Co-extrusion of multiple colors of hard candy into a single rope, as might be done for striping of starlight mints and candy canes, is also possible.

When the candy rope exits the batch roller or extruder, it enters a series of sizing wheels to bring it down to the appropriate size for the forming unit. Pairs of rotating disks (or wheels) channel the rope into exactly the right diameter (Figure 8.7). Control of temperature in both the batch roller and rope sizers is critical. If the candy mass gets too cold, it will not be sufficiently plastic and can crack as it passes through the rollers. It will also shatter as it enters the forming device if it is not sufficiently plastic.

Figure 8.6 Extrusion of hard candy (Courtesy of Sollich)

In continuous formers, the candy rope, with temperature controlled to still be in the plastic state, is fed to a machine that forms the desired shape. Numerous cutting and forming devices have been used. Ball formers, drop rollers, continuous cutters, rotary and chain-die formers are still in common use for forming hard candies from the plastic rope.

Drop rollers (Figure 8.8) are two counter-rotating rollers with sequenced depressions so that the candy fills each depression as it passes through the two rollers. A consistent candy rope from the sizing rollers is fed to the drop rollers to form the candy (e.g., lemon drops) shapes. Temperature control is critical here too since the candy mass must be sufficiently plastic to fill each depression, but still sufficiently stiff to retain the shape during cooling. A continuous candy mass comprised of drops and a thin candy webbing exit the rollers, after which it passes through a cooling tunnel to solidify the drops into a glass. Upon exiting the cooling tunnel, the drops are separated from the webbing and tumbled slightly to smooth the edges prior to packaging. Note that drop rollers have limited flexibility in candy shape and have largely been replaced by more modern methods of candy forming.

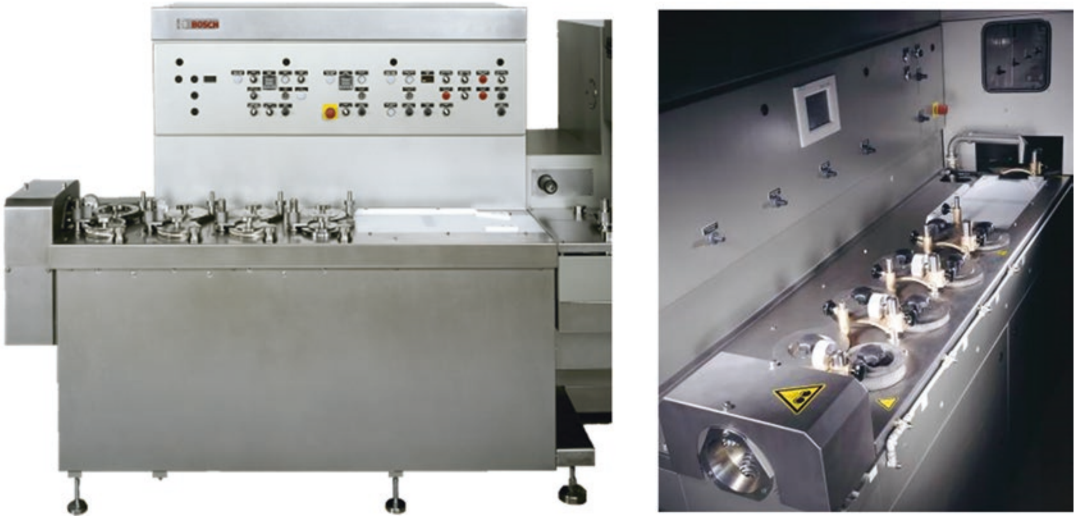

Figure 8.7 Rope sizers for hard candy (Courtesy of Bosch)

Figure 8.8 Drop roller for hard candy (Courtesy of Loynds International Ltd)

Candy pieces may also be formed from the pliable, plastic candy ropes in die-forming units. Two of the most common die-formers are the rotary die former (Figure 8.9) and the chain die former (Figure 8.10). The rotary die cutter is a series of plungers and guiding cams that cut and form the candy shape. The candy shape is controlled by the shape of the die and whatever impressions are etched on the surface of the die. The chain die former is comprised of two counter-rotating chain dies that cut and stamp the candy into the desired shapes. The candy rope may also be formed in a ball roller, which utilizes a three-roller system to make such designs as starlight mints (swirled colors on the face of a disk candy), balls or barrel-shaped candies (e.g., root beer barrels). Two cutting rollers cut perpendicular into the candy rope while a third, support roller provides the base against which the rope is cut. This forms the candy shape/design within the ball roller (Figure 8.11).

8.3.1.6 Depositing

Instead of cooling the candy mass to the plastic state and then forming, the candy may be deposited directly into molds while it is still hot and fluid (Figure 8.12) (Prange and Bond 2012). The colored and flavored candy mass is discharged into a heated hopper. The hopper must be hot enough to maintain the candy in its fluid state while metering nozzles deposit the proper amount of candy directly into a mold of the desired shape. Multiple nozzles may be employed to continuously fill wide banks of candy molds attached to a continuous conveyor. The molds are typically made of Teflon-coated metal and are indexed below the depositing head. After being filled, the molds travel through a cooling section before the finished candies are discharged from the cavities. Several discharge mechanisms exist, with spring-loaded pins set in the bottom of the mold cavities being the most common.

There are numerous advantages to depositing hard candies. Depositors typically have high production volumes with minimal labor costs. They produce uniform finished candies even with formulas containing high levels of fat or protein (products that typically tend to deform in plastic-forming machines). Because of the gentle nature of syrup handling, deposited hard candies are particularly smooth and clear, with little entrainment of air bubbles. Further, with newer depositing technologies, multicolored, multilayered, striped or even filled pieces can be made. Triple shot depositing systems are available for hard candy, where three different colors and flavors of hard candy can be co-deposited simultaneously into the mold.

Figure 8.9 Rotary die former (Courtesy of Robert Bosch GmbH)

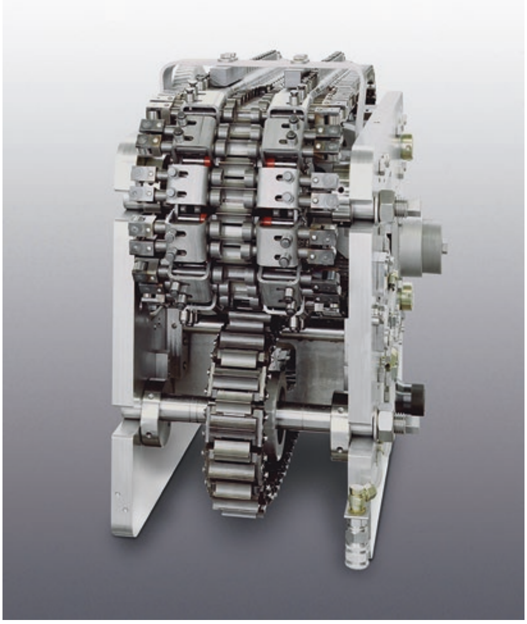

Figure 8.10 Chain die former (Courtesy of Hänsel Processing GmbH)

Figure 8.11 Ball roller: *top*, open with three sets of rollers visible; *bottom*, balls being formed (Courtesy of Proform)

On the negative side, purchasing a hard candy depositing system requires a large initial capital investment. Furthermore, due to the large number of molds on a typical conveyor, changing the candy shape on a depositor costs considerably more than changing the shape on a plastic forming machine (where typically, only a single candy die assembly is needed). This reduces the flexibility of depositing systems. While a variety of shapes can be produced, deposited candies normally have a smooth side that corresponds to the top of the piece as it sits in the mold cavity. There are potential quality issues as well with depositing systems. Due to the extended high temperature hold times in the depositing hopper, potential problems can arise due to the negative effects of heat. Inversion of sucrose occurs rapidly at elevated temperatures, particularly in the presence of organic acids. This results in softer can-

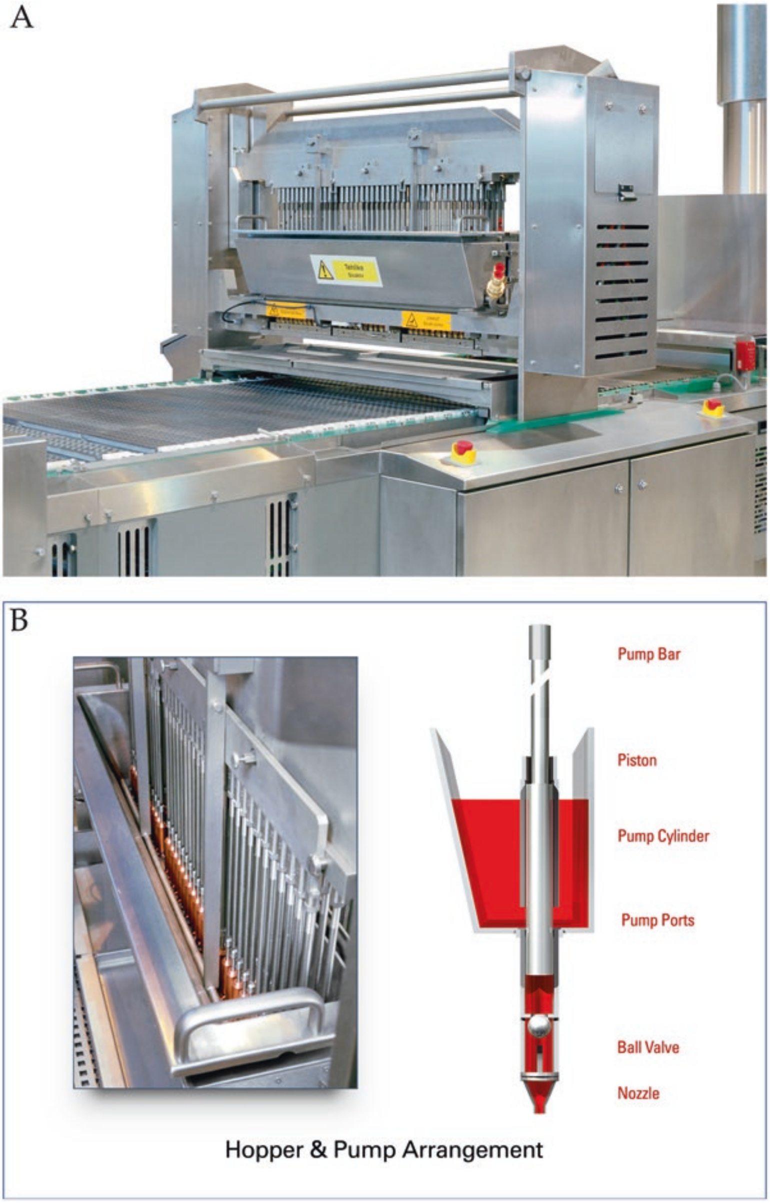

Figure 8.12 Depositing system for hard candy. (**a**) Depositor. (**b**) Depositor hopper and pump arrangement (Courtesy of Baker Perkins)

dies that may quickly become sticky during storage. Color may also be an issue, with development of yellow or brown hues. To minimize these defects, buffered acids are necessary when producing acidulated products. Holding the candy mass at high temperatures can also lead to graining of the sucrose. For this reason, higher levels of glucose syrup may often be used for deposited hard candy. Finally, because the candy mass must be quite fluid to properly fill the mold cavity, lower viscosity syrups (e.g., high maltose) must be used instead of the thicker regular conversion glucose syrups.

8.3.2 Other Hard Candy Technologies

Numerous variations of these processes for making hard candies have been developed over the years. These developments typically produce some unique aspect of hard candy, either in shape and appearance, or in some other physical aspect.

8.3.2.1 Cut Rock and Striping

To make hard candy with patterns (flowers, flags, butterflies, orange slice, etc.) or lettering within the piece (Figure 8.13), which is sometimes called "cut rock", several layers of different colored hard candy mass are placed in the correct geometrical arrangement prior to roping and cutting. The process involves arranging different colored strips of hard candy into a cylinder to create internal designs and "blocking" those shapes so they are retained when the mass is rolled into a rope (McGovern 1995). These internal designs are constructed in a cylinder of about 0.3–0.5 m (≈1.5 ft) in diameter and about 1.5 m (4–5 ft) long. When this large cylinder is rolled and spun down into a rope (perhaps 2–3 cm in diameter) by the batch roller and sizing rollers, the interior design remains throughout and can be seen in a transverse cut. Knowing exactly how the different layers of candy mass must be placed to give the desired appearance in the finished candy is a matter of considerable artistry and experience.

In England, different resort towns have their own characteristic cut rock (e.g., Brighton rock), often containing the city name formed into the candy piece. These candies are often sold in the form of long cylinders (about 2–3 cm in diameter) rather than being cut into individual pieces.

Cut rock with various internal shapes was particularly common during the Christmas holiday season, although, perhaps in part because it is hand made, this type of candy is less common now. Cut rock containing butterflies, flowers, fruit designs, flags, and many other shapes can still be found. It is also common to see corporate or university logos within specially-made cut rock (Figure 8.13).

While blocking, roping and cutting cut rock or striped candies, it is imperative that the candy mass have the proper plasticity. The candy mass needs to be maintained at a sufficiently warm temperature to maintain proper pliability for forming. Since cut rock is primarily an artisan-type candy, small batches are made using traditional hard candy methods, with the candy masses being held on warming tables until they are ready to use.

Striped candies are similar in some respects to cut rock, although striping is generally much easier than developing an interior pattern. Two common hard candies made with striping are candy canes and the traditional "starlight" mints, candy buttons with striping running along their periphery (Warnecke 1995). Starlight mints are

Figure 8.13 University of Wisconsin lettered rock hard candies with starlight mints

made by putting strips of red candy onto a core of white candy (whiteness either from aeration or more commonly, addition of titanium dioxide colorant), forming into a rope, and then cutting on a ball former (see Section 8.3.1.5) to pull down the stripes and form the colored swirl on the flat surface of the mint.

Candy canes are made in a similar fashion as starlight mints, except for the cutting process. A rope of red (or any other color) striped candy mass is formed, either with batch rollers and sizing rollers or by extrusion, but in this case a slight twist is given to the candy rope to cause the stripes to helix around the candy stick. As the rope exits the sizing roller or the die (orifice) of the extruder, it is twisted as it passes through two offset rollers. The rope is sized to the right diameter and cut into the desired lengths. While still warm, the candy rope is bent into the candy cane shape, giving it the characteristic crook. It is then cooled quickly to set the candy into the glassy state.

8.3.2.2 Aeration

Some hard candies are aerated to provide specific effects (Jones 1995). For example, aeration (1) provides a white or pastel color, (2) gives a glossy, satin-like appearance to the candy, (3) induces a crispy or crunchy finished product structure, or (4) increases product volume (decrease density) without increasing product weight. The vigorous agitation during pulling is also thought to contribute to crystal development, which affects texture (increase crunchiness) and appearance (opacity). Examples of aerated hard candies include starlight mints, candy canes, filled or honeycombed candies, and some types of cut rock.

Various methods are available to incorporate air into hard candies. Air can be incorporated by pulling a plastic candy mass (folding, stretching, refolding and restretching, etc. to incorporate air), or by continuous air injection into a liquid candy mass. Alternatively, gas can be generated directly within the candy mass by chemical reaction. Choice of technique depends on the desired effect, cost efficiency, and production rate.

Chemical aeration involves addition of bicarbonate (sodium or ammonium) to the hot candy mass, which then decomposes from the heat to generate CO_2 bubbles. As long as the bicarbonate is mixed well with the candy mass, the dispersion of small gas bubbles is quite uniform. Peanut brittle and sponge candy are often aerated in this way to decrease the density of the final product and improve eating quality by making it crunchier.

Pulling, probably the most common method of aeration, is the process of folding air into hard candies by repeated stretching, folding and layering of the candy mass. The air trapped between the folds is split into small bubbles as the mass is pulled. Air bubbles remain separate due to the high viscosity of the candy mass. Because of the high viscosity and the physical nature of pulling, the air bubbles are not spherical, but rather form irregular shapes and tubes. Several methods of pulling are available. The simplest involves pulling a candy mass by hand over a hook mounted on the wall. Although this is a low-cost, simple alternative, variability in candy quality occurs from day-to-day and between operators.

Pulling machines are often used to mechanize aeration, with both vertical and horizontal pullers available. In vertical units, the candy mass is manually placed on the top (stationary) arm and pulled by the two rotating arms operating at about 25 RPM. Some vertical units have no stationary arm, pulling the mass simply between two rotating arms. If the candy mass is too warm when loaded on the pulling machine, it flows faster than the arms can pull it back up again. On the other hand, if the candy mass is too cold when placed on the pulling machine, it does not flow very well and will not be adequately aerated. Thus, control of viscosity (based on temperature and composition) prior to pulling is critical to good aeration. Typically, the candy mass is cooled to about 95 °C (200–210 °F) for optimal pulling. Due to the vigorous mixing action, flavors and colors can also be incorporated during the pulling operation. The operator ensures consistent aeration during batch pulling by making sure the candy mass moves properly from one arm and over the next. For this reason, vertical pulling presents a safety hazard for the operator who must continually move candy mass between the rotating arms of the pulling machine, particularly during start up. A metal guard system helps keep the operator safe, but it is more difficult to load the candy for aeration and safety concerns still persist with the vertical pulling unit. Consequently, horizontal pulling machines are a much safer choice. In the horizontal puller, the operator places the candy batch in the machine, closes the guard and turns on the rotating arms, which pull and fold the candy mass in a horizontal plane. The aeration process is essentially the same as in vertical pulling, but since the natural gravitational pull on the candy mass is not used to stretch the candy, it is not as efficient as vertical pulling. Generally, longer time is required for horizontal pulling to attain similar aeration as vertical pulling. A typical pulling machine is shown in Figure 8.14.

A continuous, vertical pulling machine is available that allows the boiled candy mass to enter one end and exit as an aerated mass from the other end (Jones 1995). A series of rotating pulling arms and scraper blades allow aeration at the same time the candy mass is forced through the unit (Figure 8.15).

Additional expansion of air bubbles after pulling can be accomplished using vacuum aeration. This process can produce a highly aerated, solid foam piece with very low density. The process involves taking a pulled candy mass, forming into a rope using traditional roping and forming equipment, and then feeding the formed candies, while still warm, into a vacuum tunnel. Vacuums less than 23 in Hg (23.4 kPa absolute pressure) are used in the vacuum chamber, which causes the air bubbles to expand from six to ten times, decreasing density accordingly. In order for the candy mass to expand under vacuum, the sugar matrix must still be sufficiently plastic (low enough viscosity). However, temperature must be reduced quickly upon exiting the vacuum so that the sugar matrix sets into a glass to hold the air cells in place. The vacuum operation also contributes a small amount of moisture loss. Once the candy mass leaves the vacuum chamber, the pieces must be packaged immediately due to their propensity to pick up moisture from the environment. Malted milk ball centers are made by this process.

For higher throughputs, continuous cooking systems that incorporate air injection in a mixing tube can be used to aerate hard candies (Jones 1995). Compressed air is injected into a mixing cylinder with the liquid candy mass (immediately after it exits the cooker), with flavors and colors

Figure 8.14 Typical batch pulling machine (Courtesy of Bosch)

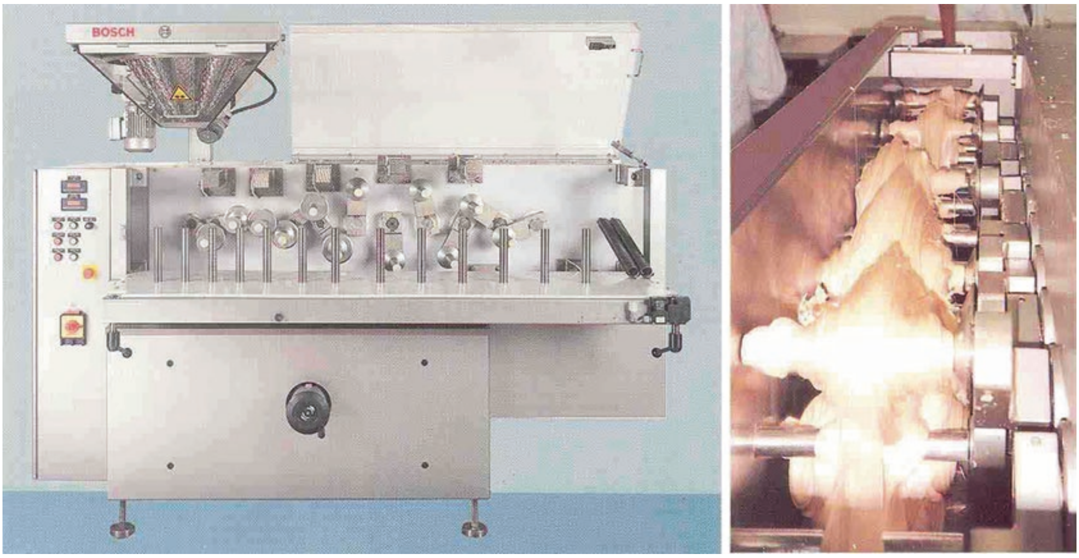

Figure 8.15 Continuous pulling machine (Courtesy of Robert Bosch GmbH)

added as desired, and the mass mixed mechanically as it flows through the unit. As with other aeration devices, it is critical to control viscosity during mixing in a continuous aerator. Candy mass viscosity is related to composition, moisture content and temperature. These parameters must all be controlled carefully in a continuous aerator to ensure efficient and uniform aeration. In continuous aerators, the nature of the injected air (free of odors, moisture, microbes, oil, etc.) as well as the injection nozzles are important to making a good aerated product. Furthermore, the mixing factors (shearing rates, RPM, etc.) within the unit influence the state of the air distribution in a candy processed on a continuous mixer. The primary advantages of the continuous aerator are that high throughput rates can be obtained with very reproducible results (minimizing variability from piece to piece). However, the extent of aeration (or reduction in density) is not as good as some other aeration techniques since the candy mass is processed at lower viscosity to minimize mixer energy requirements.

8.3.2.3 Carbonation: Popping Candy

Carbonated hard candy is made by adding pressurized CO_2 gas to the liquid candy mass. A hard candy formulation, often made with 10–30% lactose to increase glass transition temperature (T_g) and hardness, is boiled to around 152 °C (305 °F) to reduce water content to about 1–2%. The candy mass is cooled slightly (dependent on viscosity), placed in a pressure vessel, sealed, and pressurized to about 4.1 MPa (41 atm; 600 psi). Shearing during pressurization ensures that the CO_2 bubbles are quite small. In order to obtain the small bubbles (generally <10 μm) required for carbonated hard candies, the liquid candy mass must be sufficiently viscous to prevent rapid coalescence. However, if the liquid candy mass is too viscous, agitation intensity is insufficient to create small bubbles. Thus, temperature in the pressure vessel must be carefully controlled to obtain the desired carbonation level and gas droplet size.

The pressurized candy is pumped from the pressure vessel into a storage vessel, still under pressure, for cooling. These vessels are long and narrow to enhance heat transfer surface area and promote rapid cooling. As the pressurized candy mass cools to room temperature, the small CO_2 bubbles, still under pressure, become entrapped within the glass matrix. When the pressure in the storage vessel is released, the candy shatters into pieces, leaving a carbonated hard candy product. Grinding and screening are used to obtain the proper sized particle for sale.

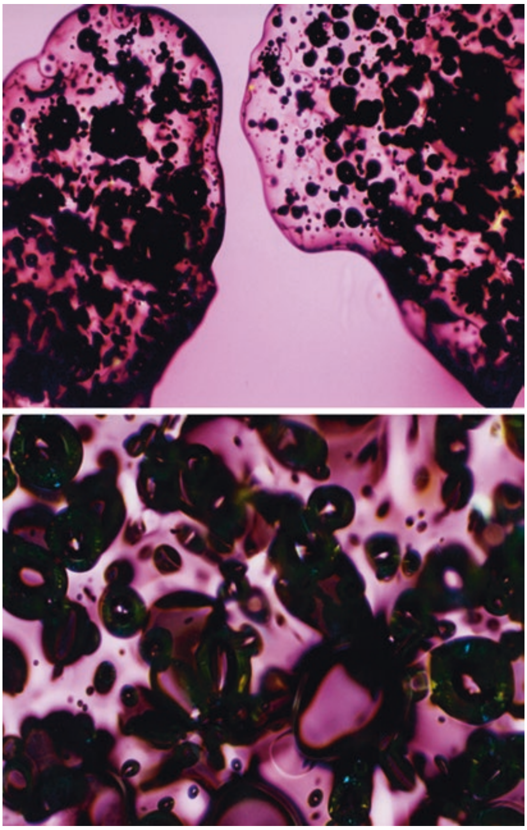

Figure 8.16 Polarized light microscope image of carbonated hard candy – small bubbles of high-pressure carbon dioxide embedded in a hard candy matrix. *Top* image at low magnification (4×); *bottom* image at higher magnification (40×)

A photomicrograph of carbonated candies, taken by polarized light microscopy, shows the small CO_2 bubbles dispersed through the solid matrix of hard candy (Figure 8.16). In these polarized optical microscope images, the dark circular shapes are CO_2 bubbles and the clear background matrix is the glassy sugar hard candy. The hardness of the sugar glass is sufficient to withstand the pressure within the small CO_2 bubbles. When the carbonated hard candy is exposed to water (e.g, through consumption), the solid matrix dissolves until the remaining glassy wall holding the pressurized CO_2 bubbles is too thin to restrain the pressure. At this point, the characteristic popping or crackling is observed as the gas shatters the thin sugar glass wall. The numerous small CO_2 bubbles pop sporadically, based on dissolution of the glass, resulting in continuous effervescence in the mouth. Popping continues until the last CO_2 bubble has popped.

Unfortunately, carbonated hard candies are extremely heat and moisture sensitive, rapidly losing their popping ability when exposed to such detrimental conditions. Both heat and moisture affect the hardness of the glassy matrix, reducing the ability of the glass to hold high-pressure CO_2 bubbles. For example, if T_g of the initial candy as manufactured is 45 °C (113 °F), when ambient or storage temperature exceeds about 40 °C (104 °F), the glass loses the brittle character necessary to hold the bubbles and the popping character quickly degrades. If storage temperature were to exceed T_g (see Section 2.9 for more discussion on glass transition temperatures), the candy would retain none of the characteristic pop as all of the CO_2 would quickly diffuse out of the amorphous candy matrix. For this reason, lactose is added to the carbonated candy formulation since its high T_g (100 °C) raises the T_g of the candy, enhancing stability. There is a limit to this approach, though, in that higher T_g also means a more brittle and sharp product. Clearly, high temperatures are the enemy of carbonated popping candy and a truly heat-resistant popping candy remains elusive. Carbonated popping candy is often coated with an edible oil and then sealed in moisture proof packaging to make them less sensitive to moisture during storage and processing.

8.3.2.4 Filled Hard Candies

Hard candies can be found with a variety of fillings, including fat-based fillings (peanut butter, chocolate, etc.), fruit-based fillings (pastes, syrups, etc.), powders (organic acids and bicarbonate), gum or chewy candy (Hintlian 1995). Although the differences in texture and taste between two components of a filled hard candy provide an interesting experience for the consumer, the process of putting a filling into a hard candy casing requires careful coordination between the two components. If viscosities and/or temperatures are not properly controlled, the results will be unsatisfactory (i.e., unfilled candies or leaking centers). Filling equipment must also be maintained in optimal working condition to ensure that each candy is sealed appropriately, with just the right amount of filling material.

A common method for inserting a filling into the center of a hard candy involves the use of a filling tube in a batch roller. This is a long pipe that extends down the entire length of the batch roller. A flexible hose is used to connect the filling tube to a pump, which draws from a filling hopper. Initially, the warm hard candy mass, still in the soft plastic state, is wrapped around the tube all the way to the discharge end of the batch roller. As the candy is spun off from the batch roller, the pump is turned on and filling is forced into the mass, essentially forming a filled tube of candy. For continuous operation, more hard candy mass can be fed into the back of the batch roller as the rotating action of the machine wraps it around the filling tube.

This type of filling operation must be carefully controlled to ensure consistent feed of both the hard candy mass and the filling so that uniformly filled candies are produced. The rope sizer must be set up to gently pull and stretch the candy so that filling is not squeezed out. Once the filled rope has been reduced to proper diameter, the candy pieces can be formed for example in a chain die former (Figure 8.10). The machine must squeeze the hard candy casing uniformly together to completely seal the filling within the hard candy casing.

The critical parameters to control for high quality filled hard candies include temperature, viscosity, and component (water, acid, etc.) migration. The temperatures of the filling and center must be about the same to ensure that no problems occur. Fillings that are too cold can cause premature solidification of the casing and lead to cracked pieces that are likely to leak filling. If the filling is too warm, it can heat the casing and lead to deformed pieces, or in the extreme, pieces where the filling bursts out of the casing. Viscosities of the casing and filling must also be controlled to prevent problems. The casing should have the proper plasticity for forming, with temperature, water content and sugar profile all being important to attaining the proper viscosity. Casings that are too hard or too soft will not process properly and will be either cracked or deformed. The viscosity of the center is also important in that it should neither be too hard or too runny to properly fill the hard candy. Finally, the filling should not transfer components, such as water or acid, to the hard candy casing. Water activity of the center should match that of the hard candy as closely as possible to minimize thermodynamic transport of moisture and subsequent degradation (softening, graining, etc.) of the hard candy. Powdered centers may contain bicarbonate and organic acids to provide a fizzy reaction when consumed. However, the two components must be kept separated, usually by encapsulating one of the powders by a fat layer. Penetration of organic acid into the hard candy casing is also undesirable as this can lead to sucrose inversion and undesired softening.

8.3.2.5 Lollipops/Sticking

Lollipops, or suckers, are essentially hard candy on a stick. They can take a variety of shapes, from round to flat or circular to heart-shaped, and a variety of sizes, from small bite-sized suckers to enormous “all-day” suckers. Lollipops can be plain hard candy or they can be filled with a different candy (e.g., chewy caramel/fudge center) or gum.

The process for making lollipops is the same process as for making hard candy, except that sticks are inserted while the candy is still relatively fluid. When making lollipops by hand, the hot fluid sugar mass is poured into molds and the stick inserted into the mold while the sugar syrup is still warm. After cooling, the hard candy solidifies around the stick and the piece is easily removed from the mold. Large-scale depositors for lollipops are now available (Prange and Bond 2012). Typical commercial manufacturers often use continuous forming and cutting (and packaging) machines specially designed to add the stick at the point when the candy is being formed. A hard candy rope (filled or unfilled) is threaded into a specially designed die former with the shape of the lollipop head. The stick is inserted just after the piece has been formed in the die, while the sugar matrix is still in the plastic state. The lollipop is then cooled quickly to attain the stable glassy state.

8.3.3 Rework

When manufacturing hard candies, it is inevitable that some pieces will be produced that do not meet specifications but are still fit for consumption (Chalmers 1985). This includes candies that are deformed, chipped or perhaps improperly flavored or not sufficiently filled. Since by far the predominant ingredients in hard candies are sugar and glucose syrup (or various polyols in the case of sugar free confections), and for the most part their basic nature has not been altered, it would be expected that a candymaker would want to somehow reuse these ingredients. The candy being reused is often referred to as "scrap", "reclaim" or more accurately "rework".

Throughout the years, several strategies have been applied to reclaim the sugar and glucose syrup in candy not deemed suitable for sale. The simplest procedure was to add the rework material directly back into subsequent batches of hard candies that have the same or complementary flavors. This would typically involve crushing or grinding the rework pieces and then adding them to a hot, cooked candy mass early enough in the process to ensure that they re-melt completely. An alternate version of this strategy would involve using the rework in a different product. For example, reworked hard candy can be added to the fillings of filled hard candies. Rework candies have even been used as toppings for bakery products. Of course, there are certain risks involved with putting rework back into candy production. With a high-sugar formula where there is the possibility of crystallization, rework may provide seed crystals that could cause graining of the fresh product. Also, there is always the risk of introducing contaminants (metal, allergens, dirt, etc.) if the rework material has not been properly handled or stored.

The direct reuse method of rework processing is best suited to smaller-scale production where there is more operator input. It does not lend itself well to a modern, high speed and high volume factory. Under those circumstances, the confectioner would normally prefer to dissolve the rework so that it can be added back earlier in the production process in liquid form. Unfortunately, often the minor ingredients, such as colors and flavors, can have a detrimental effect on subsequent production; this is especially true if acids are present.

Under these conditions, the rework must be processed to remove the other ingredients so that only sugar and glucose syrup remain. This is ordinarily accomplished by dissolving the rework in water and then using powdered activated carbon to absorb the flavors and colors. Depending on the flavor and color load and the desired purity of the resulting rework syrup, activated carbon is typically added at approximately 1% by weight of the candy solids. Once the activated carbon has been given sufficient time to absorb undesirable ingredients, the rework syrup must be treated to remove the carbon. Due to the small carbon particle size, plain traditional filters would not work well. Instead some type of filter precoat, such as diatomaceous earth, must be applied to the filter to allow for depth-type filtration. If the rework candies contained acid, then a final step would be to add a food-grade neutralizing agent (such as sodium bicarbonate or calcium carbonate) to bring the pH close to neutrality.

Treated liquid rework can be added to the fresh sugar/glucose syrup stream at any point prior to cooking. Processing issues, primarily the result of viscosity, restrict the concentration of the rework syrup to approximately 60%. This means that the rework syrup is susceptible to microbial growth and it limits how long it can be stored prior to use. Since the invert produced during the initial cooking of the candies being reworked is not removed by treatment, there is also a limit to how much rework syrup can be used before it begins to adversely affect the quality of the finished confections. Normally, this would be below 7% on a solids basis and it would need to be monitored to ensure that the reducing sugar level does not vary from established specifications (Chalmers 1985).

8.4 Product Characteristics

During processing and storage, there are numerous chemical and physical changes that take place in the candy mass. Chemical changes occur during processing due to the high temperatures to which the candy mass is exposed during boiling to reduce the water content. Physical changes also occur during processing as the water is removed and the candy mass is cooled and formed. However, additional changes can occur to both the physical properties and the chemical nature (including flavor) during storage. Storage at elevated temperature and/or relative humidity hastens these changes.

8.4.1 Chemical Changes

Numerous chemical changes occur during high temperature cooking of hard candies. The most important of these reactions include (1) inversion of sucrose into glucose and fructose, (2) browning, which leads to discoloration of the syrup, and (3) polymerization of the monosaccharides into higher saccharides. The extent of these reactions depends primarily on cook time and temperature, saccharide composition, and pH.

8.4.1.1 Inversion

Inversion, or the hydrolysis of sucrose into the monosaccharide components, fructose and glucose, occurs readily at the elevated temperatures needed to remove sufficient water to produce a stable hard candy. The rate of inversion is dependent primarily on time, temperature, and pH (see Section 1.3). Holding a candy mass for long times at high temperatures and low pH causes rapid inversion to take place. High-speed continuous cookers operated under vacuum result in inversion levels less than 1%, whereas slow batch cooking at ambient pressure may result in up to 3–5% inversion. In general, higher amounts of invert sugar in a hard candy lead to quality and shelf life problems due to the lower glass transition temperature (see Section 2.9) and greater hygroscopicity (see Section 3.5).

Inversion of sugars leads to changes in the final saccharide distribution of a finished hard candy product. That is, the finished product contains a different saccharide distribution from what was used in the formulation due primarily to sucrose inversion. Table 8.3 documents the range of saccharides found in commercial (European) hard candies (Smidova et al. 2003). The water contents match those shown previously (Table 3.1) for domestic hard candies; however, the range of saccharide compositions found provides some interesting comparisons. The sucrose content varied from a low of 32% to a high of nearly 88%. The candies that contained the lowest sucrose contents undoubtedly were made with very high levels of glucose syrup, and so had higher glucose, maltose and higher saccharide levels. The presence of glucose is primarily due to addition of glucose syrup or from inversion of sucrose although some hard candies may contain a small amount of invert sugar (to enhance flavor release). The presence of fructose is most likely due to inversion of sucrose during manufacture, although again, a small amount may be added intentionally. Candies that contained significant levels of fructose, whether from direct addition or sucrose inversion, are prone to stickiness due to its hygroscopicity.

Table 8.3 Saccharide compositional analysis of various European hard candies (From Smidova et al. 2003)

Component	Range (%)	Average (%)
Water	2.1–5.1	3.5
Fructose	0.2–8.6	2.1
Glucose	1.1–12.4	6.7
Sucrose	31.7–87.7	49.2
Maltose	0.7–33.2	7.0
Higher saccharides	12.9–44.9	30.4

8.4.1.2 Color Development

The development of brown color during cooking is generally considered a negative effect of the processes used in hard candy manufacturing. Clear, uncaramelized syrup is usually desired for the best flavor and appearance. The degradation processes that occur during cooking may be caused by two reactions, Maillard browning and caramelization of sugars, although in most hard candy cooking operations, sugar caramelization is the primary reaction responsible for color development because of the negligible protein content. Certain glucose syrups may contain small amounts of protein, providing substrate for the Maillard browning reaction, but most sugar syrups do not brown rapidly until temperatures exceed about 132 °C

(270 °F), well above the temperatures needed to initiate Maillard browning.

In both Maillard browning and caramelization, a number of parameters affect the rate of color development (see Section 1.4.3). The saccharide distribution, particularly the reducing sugar content, in the candy mass directly influences browning rate. Candies made with higher total DE (from glucose syrup addition or inversion during processing) lead to browner products. A typical target range of total DE for a hard candy is 16–18%. The time spent at high temperatures (time of cooking) also influences the development of brown colors. Batch cooked candies develop significantly more color than continuously cooked candies because of the longer processing times required to reach the final temperature (and therefore, the desired water content). In high-speed continuous cookers, the target temperature and water content may be reached in less than a minute, whereas in batch cookers, cooking times may be as long as 15–30 min. Vacuum operation also affects color formation since lower cooking temperatures and shorter processing times can be used to attain the desired final moisture content.

Water content can also affect the outcome of browning reactions. Sugar caramelization is actually a combination of several reaction steps that lead to formation of colors and flavors. The first step of caramelization involves the dehydration of sugar into an anhydro form. These anhydro sugars can undergo numerous reactions, including ring formation and polymerization (or reversion). The high molecular weight polymerization compounds, including caramelans ($C_{24}H_{36}O_{18}$), caramelens ($C_{36}H_{50}O_{25}$) and caramelins ($C_{125}H_{188}O_{80}$), are responsible for the brown caramel color formed during cooking of sugars. Numerous flavor molecules are also formed, including diacetyl, hydroxymethylfurfural (HMF), hydroxyacetylfuran (HAF), hydroxydimethylfuranone (HDF), dihydroxydimethylfuranone (DDF), maltol and hydroxymaltol. Sugar source (e.g., impurity types and levels) and pH also affect the rate of caramelization and the nature of the compounds formed. For more details, see Section 1.4.3.

8.4.1.3 Reversion

Reversion, or polymerization, of glucose and/or fructose may also occur under conditions found during cooking of hard candy masses. Polymerization products that may be formed include polydextrose and polyfructose. Numerous studies have investigated the polymerization of monosaccharides, particularly dextrose, under acidic conditions. Pilath et al. (2010) characterized the mechanisms and kinetics of dextrose reversion and found that only disaccharides were formed at mildly acidic conditions with low (12%) dextrose levels.

Studies specific to conditions pertinent in candy manufacturing are generally lacking. One study, by Sabbagh and Fagerson (1979), investigated the changes in saccharide composition during processing of hard candies by use of gel permeation and ion exchange chromatography. To follow the formation of reversion products from fructose and glucose, radioactively labeled fructose and glucose were added to the hard candy mixture (sucrose, invert sugar and 42 DE glucose syrup). The candies were cooked under vacuum to a moisture content of 2.1%. Saccharide distribution analysis showed that glucose did not undergo polymerization under the experimental conditions used, but that several reversion products of fructose were formed. At least three different fructose polymers between di- and trisaccharides were found in the cooked candies, indicating polymerization of fructose had occurred during processing. These results clearly show that reversion, or polymerization of monosaccharides, can occur during hard candy manufacture. These reversion products affect physical properties since they increase T_g and act as crystallization inhibitors. In this sense, some reversion products are undoubtedly desired, although too much reversion might negatively impact the physical and sensory properties of the hard candies.

8.4.2 Microstructure

Hard candy is a sugar glass made by concentrating the sugar syrup and cooling it rapidly into an amorphous state below its glass transition temperature (Hartel 2012). Sugar crystallization during cooling and forming is prevented by a combination of the reduced molecular mobility (and high viscosity) and the addition of doctoring agents that replace some of the sucrose, thereby reducing its relative concentration. Doctoring agents like glucose syrup and invert sugar impede the formation of sucrose crystals and allow more time that the candy mass can be worked before crystallization occurs. Figure 8.17 shows schematically how the various molecules present in hard candy are organized in a sugar glass. The close proximity of these molecules substantially reduces molecular motion, both translationally (from point to point) and rotationally (rotating on an axis).

From a molecular standpoint, there are several factors that influence the formation of a sugar glass and the subsequent stability of hard candy. These include the type and relative concentrations of the sugar molecules used, addition of other components, and the amount of water remaining after concentration. These components influence the glass transition temperature (T_g) of the final mass, which determines its physical state. T_g is the point where the sugar mass transforms from an amorphous fluid with high viscosity into a glass with characteristics of a solid (does not flow) (see Section 2.9). Although this transition technically occurs over a temperature range and there is not a single distinct transition point, a single temperature is usually given as an indication that the transition has occurred. The use of a single T_g allows us to discuss the stability of a hard candy sugar glass relative to the actual temperature of the candy. If the actual temperature of the hard candy is above its T_g, it is susceptible to flow. The higher the temperature above T_g, the softer the product and more likely it is to experience flow. If the temperature of the hard candy were sufficiently above its T_g, it would become liquid once again and flow. Hard candy held at temperatures below T_g is stable for long periods of time even though it is not in an equilibrium state. The kinetics of change (either physical or chemical) when temperature is below T_g are extremely slow and shelf lives of two or more years are not uncommon.

T_g values for various sweeteners were shown in Table 2.7. The T_g of pure sucrose is between 65

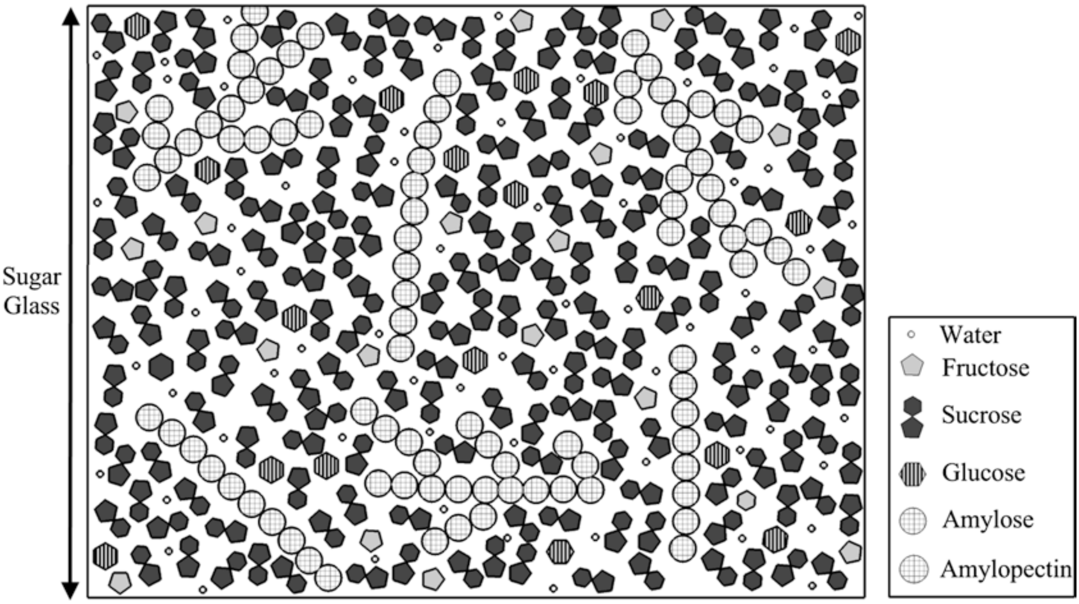

Figure 8.17 Schematic of molecular arrangement in hard candy as a sugar glass. Shown are water (*small dots*), fructose (*pentagons*), glucose (*hexagons*), sucrose (*pentagon-hexagon doubles*), amylose (*linear chains*) and amylopectin (branched chains) (With permission from Hartel et al. 2008)

and 70 °C (149–158 °F) so that technically a stable hard candy can be made that contains just sucrose. However, to prevent sugar crystallization, both during the manufacturing process and during storage, "doctoring" agents like glucose syrup and invert sugar are typically added to the formulation or generated during the process through choice of operating conditions. The type and amount of glucose syrup added to the formulation influences the stability of the hard candy through its effect on T_g as well as on inhibition of sucrose crystallization. A typical 42 DE glucose syrup has a T_g slightly higher than sucrose, so its addition in a hard candy formulation results in a slight increase of T_g of the final product for a given moisture content (see Table 2.8). However, different glucose syrups have different saccharide distributions, which can influence the T_g of hard candies. Glucose syrups of different conversion (DE) also have different T_g. In general, higher DE glucose syrups result in lower T_g, and vice versa, since smaller molecular weight materials generally have lower T_g. Thus, to increase T_g of a hard candy, use of a lower DE glucose syrup would be recommended. However, other parameters are also affected by choice of glucose syrup, including color changes, sweetness, hardness, viscosity, machinability, and, of course, finished product cost. Therefore, the choice of glucose syrup to use in hard candy must be based on numerous considerations, not just its effect on T_g.

Commercial hard candies, with water content in the range from 2% to 4%, typically have T_g values anywhere from 25 to 45°C (77–113 °F), depending on the sugar composition and water content. Candies with low T_g values, closer to room temperature, are generally the most unstable. If ambient temperatures rise above T_g, which might happen for example in the summer in warm environments, these candies are very unstable and often exhibit cold flow and stickiness. The most stable hard candies typically have T_g values between 40 and 45 °C (104–113 °F), well above most ambient temperature conditions. When T_g values are higher than 50 °C (122 °F), however, the hard candies become too hard and brittle, almost sharp-edged, and do not dissolve easily in the mouth. Although candies with such a high T_g would be quite stable, their sensory characteristics are generally not acceptable. Thus, the appropriate T_g for hard candy falls within a fairly narrow range.

Table 8.4 Moisture contents and glass transition temperatures of some commercial hard candies purchased from the grocery store (Nowakowski 2000)

Sample	Moisture content (%)	Glass transition temperature (°C)
Brand 1 – 5 flavors	4.1 ± 1.0	26.6 ± 2.2
Brand 2 – 5 flavors	3.5 ± 1.0	40.3 ± 4.4
Brand 2 – Sour balls	2.8 ± 0.5	41.2 ± 1.6
Brand 2 – Blue mints	4.8 ± 0.9	33.2 ± 0.5
Brand 3 – Wild cherry	3.8	37.1
Brand 4 – Cherry	1.7	40.2
Brand 5 – Throat lozenges	3.8 ± 2.5	36.3 ± 0.4

Water content and T_g of some commercial hard candies, obtained at random from retail outlets, are shown in Table 8.4. Moisture contents varied from 1.7% to 4.8%, with T_g values from 26.6 to 41.2 °C (80–106 °F). A T_g of 26.6 °C (89 °F) is close to room temperature (≈22 °C; 72 °F), meaning that this particular candy was extremely unstable. Small increases in moisture content, caused for example by diffusion through the package, would lead to the undesirable lowering of T_g in the candy piece. In particular, this candy was prone to a sticky layer at the surface where the wrapper was difficult to remove from the candy. In contrast, a T_g on the order of 40–45 °C (104–113 °F) is indicative of a relatively stable hard candy. Only in the warmest environments, as might be found on hot days in some parts of the country or in unrefrigerated shipping conditions, would T_g be exceeded, at which point even this product would become fluid and sticky.

Sugar-free hard candies are also generally in the glassy state (although interestingly the original sugar-free hard candy based on sorbitol was actually crystalline). Glassy sugar-free hard candies follow the same principles in terms of microstructure and stability as sugar-based hard candies. However, many of the more common polyols (particularly sorbitol) have T_g values below room temperature (see Table 2.7), making them unacceptable for use in glassy hard candies. As stated previously, when T_g of a hard candy is below room temperature, it is not in the glassy state and is prone to cold flow. The lower the T_g, the more likely cold flow is to occur. To prevent this, sugar-free hard candies are often made from either isomalt, which has a sufficiently high T_g (about 64 °C; 147 °F), or a mixture of maltitol and HSH, which also have T_g values greater than room temperature.

8.4.3 Stability/Shelf Life

Since hard candies typically have a water activity less than 0.3 (Ergun et al. 2010), microbial issues are not a problem during storage. The low water content in hard candy ensures that no microorganisms can grow. However, sugar glasses are notoriously hygroscopic and readily pick up moisture from humid air. The equilibrium relative humidity (ERH) of a typical commercial hard candy is often quoted as being 20–30%, meaning that a hard candy exposed to ambient air with relative humidity greater than about 30% readily picks up moisture from the air. Moisture sorption would continue until the vapor pressure of water above the candy equilibrates with the vapor pressure of water in the air. Moisture uptake can lead to several problems in hard candies, namely stickiness, graining, and flavor loss.

8.4.3.1 Stickiness

Early work by Makower and Dye (1956) on moisture sorption showed that pure sucrose glasses readily picked up moisture from the surrounding air, with the extent and rate of uptake increasing with the humidity of the air. In this study, even storage at less than 5% relative humidity led to a significant increase in water content as the water molecules in the air and candy equilibrated. As expected, storage at higher relative humidity led to increased moisture content.

Water uptake into hard candy involves two steps. First, water molecules in the air adsorb to the sugar molecules at the surface through hydrogen bonding interactions. Once water molecules are at the surface, they can slowly diffuse into the sugar glass because of the difference in water content between surface and center. Water migration into the bulk of a sugar glass (hard candy) is extremely slow; it may take well over a month for a sugar glass exposed to humid air to approach equilibrium in terms of moisture content throughout the piece. However, well before full equilibration takes place, changes at the surface are likely to have caused the end of shelf life for a hard candy. Since moisture migration to the interior of the candy is relatively slow compared to absorption of water molecules to the surface, there is a moisture gradient from the surface (higher moisture, amorphous, sticky state) to the center (low moisture, glassy state). Figure 8.18 shows schematically how water molecules slowly penetrate into a hard candy glass. Because diffusion is slow, a fairly sharp demarcation is seen between the high moisture content surface layer and interior glass. On a sealed microscope slide containing a sugar glass exposed on one edge to humid air, a moisture front can be seen working its way into the glass (Figure 8.19). Over time, moisture continues to move into the interior until eventually, the entire piece comes to equilibrium with the moisture in the surrounding air. Before moisture equilibration can occur, however, defects associated with moisture uptake at the surface of the hard candy lead to the end of shelf life.

One problem that could lead to end of shelf life is surface stickiness. Removing the plastic packaging from a hard candy that has a sticky surface is the first indication of moisture migration. This is the early stage of moisture sorption, where the surface is sticky but the bulk may still be in good shape (glassy). Typically, this problem is observed in hard candies that are low in sucrose and high in glucose syrup (crystallization inhibitor). Even though the average T_g of hard candy may be higher with addition of glucose syrup, moisture uptake is generally promoted due to the presence of the hygroscopic low molecular weight sugars (primarily glucose). When the surface gets sufficiently moist, the viscosity of the surface layer decreases to the sticky point and problems occur. Actually, this process (development of a sticky

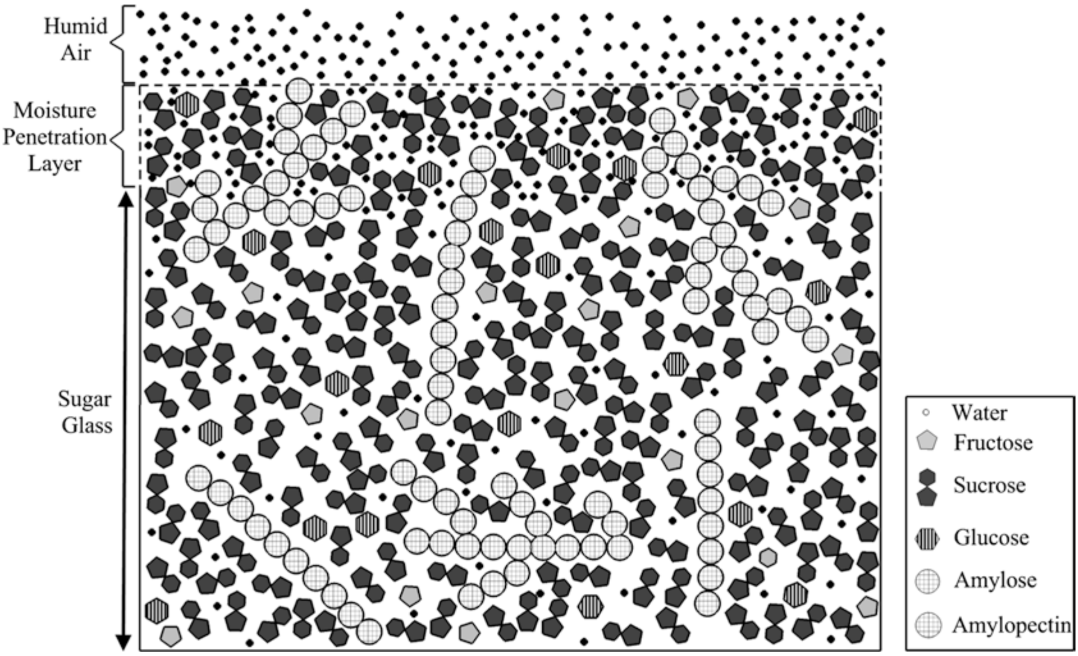

Figure 8.18 Schematic of moisture penetration into hard candy when exposed to humid air. Shown are water (*small dots*), fructose (*pentagons*), glucose (*hexagons*), sucrose (*pentagon-hexagon doubles*), amylose (*linear chains*) and amylopectin (*branched chains*) (With permission from Hartel et al. 2008)

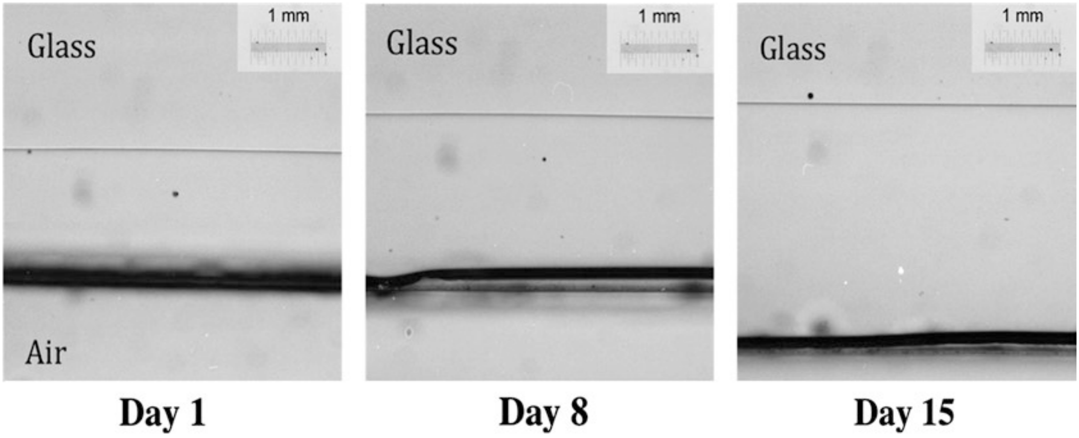

Figure 8.19 Movement of a moisture front through a thin layer of sugar glass when exposed to air of 75% relative humidity. The sharp thin line (due to refractive index differences) penetrating into the sugar glass separates the surface layer with higher moisture content from the interior intact glass (With permission from Hartel et al. 2008)

surface) can happen even without moisture sorption. All that needs to occur is for the ambient temperature to increase to a point above T_g. Both processes leading to stickiness can be seen on a state diagram (Figure 8.20), where either moisture sorption during storage (point A to point B) or temperature increase (point A to point C) can lead to a condition where the candy T_g is less than ambient temperature and the sticky point is reached. In general, the sticky point of sugars falls at temperatures about 10 °C higher than their T_g values (Wallack and King 1988), where viscosity

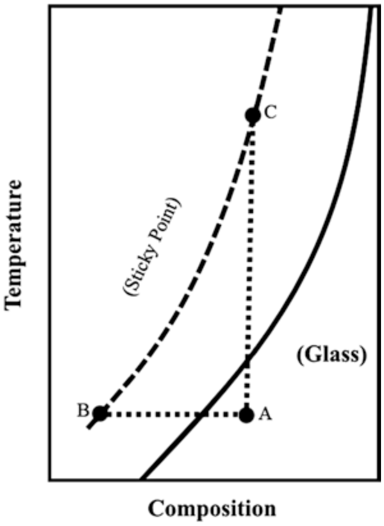

Figure 8.20 Instability of hard candy due to either moisture sorption or temperature increase. Hard candy can become sticky by either a moisture increase (**a**, **b**) or a temperature rise (**a**–**c**)

has been reduced to about 10^8 Pa-s (down from about 10^{12} Pa-s at T_g). Again, this sticky layer forms on the surface of the candy while the interior retains its original glassy character, at least for a while. Over time, this high moisture syrup layer penetrates into the interior of the candy piece as the entire candy strives towards moisture equilibrium.

8.4.3.2 Crystallization (or graining)

In hard candies with higher sucrose content (above about 70% sucrose), graining (sugar crystallization) is more of a concern than stickiness (although stickiness may still occur) during moisture uptake. The lack of corn syrup as an inhibitor allows the sucrose to crystallize as moisture penetrates the surface. Makower and Dye (1956) observed crystallization of pure sucrose glasses as a function of storage humidity and time. Storage at relative humidity less than 12% did not result in graining for nearly 2 years. The amount of moisture picked up at this low RH did not lead to a sufficient increase in molecular mobility for crystallization to occur or said another way, that level of moisture did not drop T_g of the surface below storage temperature. At a relative humidity of about 16%, crystallization was observed after 300 days of storage. Storage at higher relative humidity led to faster crystallization to the point where exposure to a relative humidity of 30% led to crystallization within a few days. The moisture at the surface reduced T_g and increased molecular mobility sufficiently so that nucleation could occur. That is, the sugar molecules must have sufficient mobility that they can rearrange and reorient themselves with their neighbors into the crystalline state. Sucrose crystallization occurs initially at the candy surface where the moisture content is highest.

Once crystals form at the surface and begin to grow, the sugar concentration in the vicinity of the growing crystal decreases. This layer then has substantially higher water content than the interior candy and moisture migration into the piece is accelerated (compared to when no graining has occurred). In addition, the elevated water content at the surface of the piece due to graining now leads to a reversal of the original driving force for moisture sorption so that water actually is driven out of the piece into the surrounding air. This leaves a high moisture content (syrup) layer to move into the piece causing additional crystals to form (Figure 8.21b) until eventually the entire piece has grained through from surface to interior.

In some hard candies, a few small sugar crystals may be imbedded in the glassy matrix due to improper handling during manufacture. One study (Smidova et al. 2003) showed that many of the commercial candies (in Europe) studied contained small amounts (1–3%) of crystalline sucrose. When sucrose crystals are present within the glassy matrix, they are stable (do not grow) as long as the candy remains below T_g. However, the crystals start to grow when temperature increases above T_g, with the rate of growth proportional to how far the temperature increases above T_g. The mobility of sucrose molecules is then sufficiently high that crystal growth can proceed and the crystals get larger, as seen in Figure 8.21a. This phenomenon has been called "internal" graining since moisture sorption at the surface is not needed to promote crystal growth.

Graining has several consequences of concern to candy quality. First, the appearance changes. Dye molecules are excluded from the growing

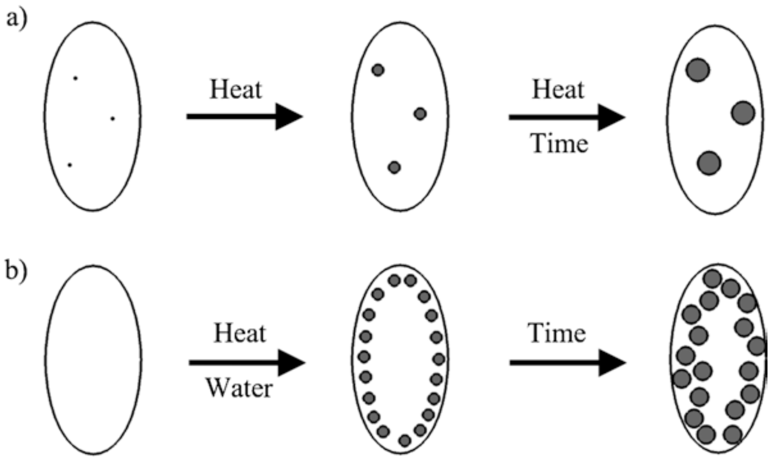

Figure 8.21 Dry (**a**) and wet (**b**) graining in hard candies (With permission from Hartel 2001)

crystals and become concentrated in the liquid regions remaining between the crystalline matrix. This typically gives a mottled appearance or a dull, opaque coloring. Second, the formation of crystals surrounded by a fluid matrix causes a change in physical characteristic or hardness. A grained hard candy has a significantly softer texture and requires less force to penetrate. A fresh hard candy in the glassy state is sufficiently hard (and brittle) that a fingernail does not penetrate at all. Once graining has occurred, the fingernail can easily penetrate, with the depth being related to the extent of graining.

The principles for graining of sucrose in hard candies apply equally as well in sugar-free versions. Hard candies made with either isomalt or lactitol grain in much the same way when exposed to high humidity (McFetridge et al. 2004). Moisture from the atmosphere penetrates into the polyol matrix, reducing T_g and increasing mobility to the point where the molecules can rearrange into the crystalline lattice.

8.4.3.3 Flavor Loss

The final characteristic of a hard candy that changes during storage is flavor. Flavor loss in a hard candy is associated with increased mobility of the flavor molecules due to storage conditions. As long as the hard candy remains in the glassy state, mobility of flavor molecules is quite low and most of the initial flavor is retained (curve A in Figure 8.22). Once the hard candy is above its T_g (either through temperature increase or moisture sorption), the mobility of the flavor molecules increases. The extent of increased mobility is strongly correlated to the temperature difference above T_g. The farther the piece is from its T_g, the more rapid the loss of flavor. In the case where a hard candy is no longer in the glassy state, but does not grain, flavor loss follows curve B in Figure 8.22. Flavor loss is initially rapid, but then some residual flavor level is reached at long times. In contrast, when graining occurs in the hard candy, flavor loss is rapid and almost complete (curve C in Figure 8.22). The concentration effect of sugar crystallization increases the driving force for flavor molecule migration out of the piece and flavor loss is substantial.

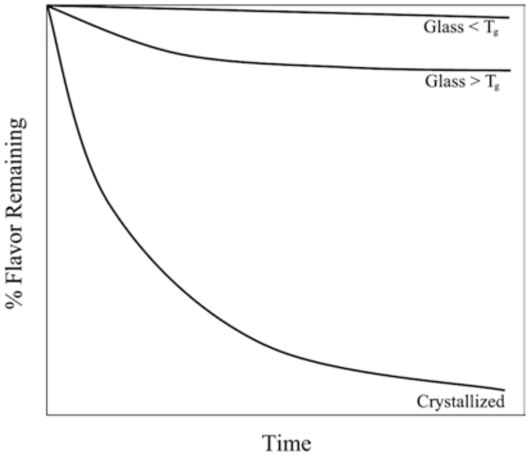

Figure 8.22 Fractional loss of flavor molecules in hard candy based on the nature of the matrix (Adapted from Levi and Karel 1995)

8.5 Trouble Shooting

High quality hard candies have excellent appearance and eating characteristics, with extended shelf life (see Section 8.4.3). Unfortunately, there are numerous ways in which these qualities can be compromised, leaving a candy with less than desirable quality (Chalmers 1983).

8.5.1 Appearance

Hard candy defects attributed to appearance include such characteristics as shape, gloss, color, breakage (cracking and chipping), dustiness and graining. Filled hard candies may also suffer from leakage of the center.

After forming, hard candy should retain its desired shape indefinitely. If the candy piece has deformed in some way, it is usually related to problems during forming or the cooling step immediately after forming. It is imperative that the cooked candy mass be cooled to the proper plastic state for forming (when not depositing). If the candy is too warm when it is formed, the piece will not hold its shape on the cooling conveyor. Instead of a ball, for example, a piece with a flat spot will be formed where flow continued after forming. In addition, if the candy rope is too large or too small, the shape will not be correct, being either oversized or undersized, respectively.

Hard candy should have a shiny surface, with an appealing gloss. This is especially true of pulled hard candies. If the surface does not have good gloss, usually the problem relates to moisture, either that there was too much left in the batch after cooking or the humidity in the processing area was too high.

Color is one of the primary selling points of hard candy. Improperly colored candy can result from a number of different causes. Assuming that the proper amount and type of color was added to the batch after cooking, off-color problems can arise either from chemical reactions involving the colors themselves or due to brown color development during cooking. Excessive holding times at elevated temperatures leads to brown color formation through caramelization of the sugars. These brown pigments can interfere with the normal colorant to give undesirable appearance. Some colorants may change characteristics if certain conditions, such as pH, are not kept consistent. Color fading during storage due to light exposure may also be a concern (see Table 8.2 for stability of various colors).

Damaged candies are unsightly and if caught prior to shipping will end up in the rework bin. Surface cracking of hard candy often occurs when temperatures during processing are not sufficiently warm to maintain a pliable candy during forming. Heaters are needed on surfaces where candy is held. If the surface of the candy mass gets too cold before the candy can be formed, subsequent stretching and forming of that candy mass leads to cracking. Broken, chipped or dusty candy typically occurs either due to rough handling, humidity too low or improper formulation. Hard candy is a sugar glass and must be treated accordingly so that it does not break or shatter. Dropping candy pieces onto a hard surface is likely to cause chipping and broken candy pieces. Using padded surfaces or decreasing the height that the piece must fall can rectify this problem. If hard candy is packaged under extremely dry conditions or if the formulation is such that T_g is too high, dusting can occur as the hard candy abrades on contact surfaces.

As noted earlier (Section 8.3.2.4), both the hard candy shell and the filling must have the proper temperature and viscosity during filling and forming in order to ensure that each candy piece is sealed properly during cutting. If not, improperly sealed candy pieces lead to leaking of the filling into the surroundings. Not only is the leaking candy unsightly, but the leaked filling can get on the surfaces of neighboring candy pieces and equipment surfaces, causing pieces to stick together and to the equipment surfaces.

8.5.2 Eating Quality

According to Chalmers (1983), eating quality is related to flavor, acidulation, texture, freshness and purity of hard candies. A candy with a well-balanced flavor provides an enjoyable eating experience and keeps the consumer coming back for more.

Flavor is arguably one of the primary concerns of the consumer. In Section 8.2.2, flavor as an ingredient in hard candy was discussed. Of primary concern is that the balance of the flavor is maintained throughout the manufacturing process. A potential cause of imbalanced flavor includes adding the flavor while the batch is too hot. In addition to potential chemical changes at high temperatures that alter the flavor chemistry, it is also likely that some components of the flavor will vaporize at different rates than other components due to differences in volatility. In addition, to ensure the best flavor, only fresh ingredients (particularly the flavors, but fats, nuts and other ingredients as well) should be used. Many flavors degrade over time during storage; thus, flavors should be used as fresh as possible to ensure the highest quality hard candy flavor.

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Fondants and Creams

9

9.1 Introduction

Fondant is a partially crystalline (and therefore, also partially liquid) confectionery ingredient with numerous small sugar crystals held together by a saturated sugar syrup. It is one of the oldest forms of confections. Possibly the earliest version of a fondant-type product is crystallized honey, where a portion of the glucose found in honey was crystallized into numerous small particles. The high crystalline content of fondant imparts a solid-like characteristic dependent on the nature of the crystal dispersion.

Typically water content in fondant may be in the range of 10–15%, although slightly lower or higher values may sometimes be found. Water is one of the most important components since it affects the hardness of the fondant, with higher water content giving a softer and runnier fondant. A softer fondant can also be produced by addition of crystallization modifiers like corn syrup, invert sugar, glycerol or sorbitol. These components contribute to the liquid phase, increasing the dissolved solids in the syrup phase and decreasing the amount of sugar crystals in the fondant.

Approximately 45–60% of the mass of fondant is in the form of small sugar crystals, which are held together by a solution phase that contains all the water and various dissolved sugars (sucrose, corn syrup, other texture modifiers, etc.). Product characteristics are determined by the relative amounts of crystalline and solution phases, the concentration of the solution phase, and the nature of the crystalline dispersion (e.g., crystal size distribution). In a good fondant, the sucrose crystals cannot be detected in the mouth because they are all smaller than some threshold detection limit (typically given as about 20 μm). Thus, controlling sugar crystallization is key to ensuring a high quality fondant product.

Fondant is used in a variety of confections and confectionery applications. It is most often used as the base material to make cream candies coated in chocolate. Fondant is also used as the starting point for other products, like frosting and icing for use on baked goods, and is often used itself as a coating or icing for cakes and other pastries. Fondant is also used to seed crystallization in confections like fudge or chewy candies. Seeding with fondant helps control formation of the proper size and dispersion of sugar crystals in these products, characteristics that are important to their overall quality.

Creams (sometimes called crèmes) are typically, but not exclusively, differentiated from fondant by the addition of frappé, an aerated sugar product. The numerous small air bubbles in frappé, which resembles a highly aerated marshmallow, decrease density and give creams a lighter texture than fondant. Creams also gener-

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ally contain colors and flavorings, along with some invertase to provide softening over time.

Cream candies may either be cast in molds or extruded and cut. Cast creams are made by warming fondant with a thinning syrup (often called "bob" syrup) to a fluid state, adding frappé, flavorings and any other ingredients. Cast creams are formed by depositing the fluid cream into a mold that has the desired candy shape. Either starch or starchless molding (Section 9.3.3.1) can be used to form cast creams. One-shot depositing technology (see Section 15.6.1) may be used to form a cream within a chocolate coating through controlled depositing of both cream center and chocolate outer at the same time. Extruded creams, or cream pastes, may be made from hard fondant at low water content softened by invertase, but more often are made by mixing powdered icing or fondant sugar with a syrup binder to form a dough or paste. The dough is then either rolled and stamped into the desired shapes or extruded and cut to form the pieces.

Creams vary in consistency from soft and runny to firm and hard, depending mostly on water content and use of humectants. A hard cream center can be softened through use of the enzyme invertase in a process often called cordialization due to its use in making Cordial Cherries. Details of this process are covered in Section 9.4.2.

9.2 Formulations and Ingredients

Fondant is a relatively simple confection, composed primarily of sucrose, glucose syrup and water. Other ingredients, like invert sugar or polyols, may be added to moderate texture and shelf life. Colors and flavors are added to suit. Frappé, a whipped sugar/glucose syrup product, is added to creams to reduce density and provide a lighter texture. At times, the enzyme invertase is added to either fondants or creams to promote softening over time (see Section 9.4.2). Typical formulations for fondants and creams are shown in Tables 9.1, 9.2, and 9.3.

Table 9.1 Typical batch formulations (in %) for fondants

	Fondant	Sugar-free fondant
Water	20	20
Sucrose	64–71	–
Maltitol	–	70
Glucose syrup[a]	9–16	–
HSH[b]	–	10

[a] 80% dissolved solids, 20% water

[b] Hydrogenated starch hydrolysate: 75% dissolved solids, 25% water

Table 9.2 Typical batch formulation (in %) for cast (deposited) cream

	Cast (deposited) cream
Fondant[a]	40–45
Thinning syrup[b]	34–38
Frappé[c]	10–25
Flavor	0.2–0.5
Color	0.1–0.2
Invertase	0–0.3

[a] Typically, 90:10 sucrose:glucose (solids basis)

[b] Thinning syrup: 40% sucrose, 26.7% 42 DE glucose syrup, 13.3% invert sugar, 20% water; cooked to 115.5–116.7 °C (240–242 °F) to give 10–12% moisture

[c] Frappé: 87% 62 DE glucose syrup, 0.6% egg albumen (dry), 0.7% water; whipped to density of 0.3 g/mL

9.2.1 Crystalline Sweetener

The primary sweetener in fondants and creams provides the bulk (typically 70–90%) of the candy mass. Numerous small sweetener crystals are dispersed throughout the candy, while some of the sweetener is also dissolved (to saturation) in the liquid phase. For fondants made by crystallizing the sweetener, two key criteria are the ease of crystallization and the saturation concentration. Sucrose is the traditional sugar used for crystallizing fondant since it has high solubility and crystallizes readily. Use of glucose or fructose as the crystallizing sweetener in fondants and creams is limited since their crystallization rates are too slow. In sugar-free products, maltitol and isomalt are often used as the crystallizing sweetener. In extruded creams, almost any fine powdered sweetener (sucrose, glucose, fructose, maltitol, isomalt, etc.) may be used since crystallization during processing is not necessary.

Table 9.3 Typical batch formulation (in %) for extruded (roll) cream

	Extruded (roll) cream
Fondant sugar	80–85
Water	8–10
Fat	4–8
Flavor	0.2–0.5
Color	0.05–0.1
Invertase	0–0.3

9.2.2 Doctoring Agent/Crystallization Control Additive

Sucrose alone would not make an acceptable crystallized fondant since too much crystallization would occur – the result would be a hard, crumbly mass of sugar. Typically, glucose syrup is added to fondant (10% is common, but may be up to about 30%) to moderate sucrose crystallization and thereby, control texture. The ratio of sucrose to glucose syrup in fondant determines the amount of sucrose crystallinity and thus, significantly affects fondant texture. Fondant made with high sucrose to glucose syrup ratio has high crystalline content and low dissolved solids in the aqueous phase, resulting in a firmer, more brittle fondant than one made with higher glucose syrup content. Increased glucose syrup level also influences shelf stability since the lower molecular weight sugars in glucose syrup give a lower water activity (compared to sucrose) for given water content, which can protect against mold growth. Moisture loss during storage is also reduced with use of more glucose syrup in the formulation. Invert sugar has similar effect as glucose syrup in controlling sucrose crystallization, but has even greater effect on moisture (and so falls under the category of humectant).

Traditionally, 42 DE glucose syrup is used in fondant manufacture to control sucrose crystallization and moderate fondant texture. Glucose syrup also moderates fondant water activity since the glucose syrup solids are retained in the liquid phase of the fondant, raising its concentration. Use of a lower DE glucose syrup gives a harder and more viscous fondant, since the liquid phase has a higher viscosity. In contrast, use of a higher DE glucose syrup (or high fructose corn syrup) gives a softer fondant since the liquid phase is less viscous, but it would also be more hygroscopic. Use of a high DE glucose syrup moderates sucrose crystallization, but also provides humectant properties (see next section).

In sugar-free fondants, hydrogenated starch hydrolysates (or maltitol syrups) are often used in the same way as glucose syrup is used in sugar-based fondants. The diverse molecular nature of maltitol syrups (the wide range of molecular weight polyols) helps inhibit crystallization of the primary sweetener (isomalt, maltitol, lactitol, etc.).

9.2.3 Humectants, Texture and Shelf Life Enhancers

Sometimes other ingredients are added to provide specific enhancements. For example, humectants such as invert sugar, sorbitol and glycerol may be used (at up to a few percent) to modify texture and storage properties. Humectants, defined as materials that promote retention of water, give a more tender texture to fondant, in part by decreasing crystallinity in the same way as glucose syrup (see Section 9.2.2), but also by causing a substantial decrease in water activity. The reduced water activity helps protect against mold growth and moisture loss of the final product. Besides their humectant properties, texture enhancers also soften the fondant by reducing the viscosity of the liquid phase.

9.2.4 Flavors

The choice of flavor in a fondant or cream is based on the desired effect, and a wide range of flavored products is available. Mint is often a highly desired flavoring in fondants and creams since mint flavors are sufficiently strong to offset the sweetness of the high sugar content. The "cooling" sensation of mint flavors, especially in the center of chocolate-covered creams, can also offset the sweetness and extend the flavor sensation.

Other various flavors also can be found in cream centers, from maple syrup to cherry cordial.

Typically, liquid flavors are added late in the process to minimize flavor degradation during heating. For example, flavor may be blended into the fluid fondant (e.g., in an in-line mixer or separate mixing tube) after it exits the fondant beater, just prior to cooling and solidification. The liquid flavors are usually water soluble and dilute enough to be totally dissolved into the fondant or cream matrix. Oil-soluble flavors may be used in creams with higher fat content to ensure the flavor is more fully incorporated into the cream. In the case of fruit flavors (citrus, berry, etc.), a slight amount of acid is often added to the fluid fondant to increase the flavor impact and enhance the nuances of the flavor. As always, flavors need to be stored properly prior to use in order to provide fresh flavor for enhanced shelf life of the fondant or cream.

Natural flavors (fruit purees, etc.) are often used at slightly higher levels than synthetic flavors. These ingredients also provide coloring to creams.

9.2.5 Colors

Both artificial and natural (exempt from certification) colors may be used to provide distinctive fondants and creams. Because of the relatively higher water content, either certified dyes or lakes may be used. Water-soluble natural pigments would also find application in creams.

Colors based in sugar syrups (solutions or dispersions) can be helpful so as not to lower the solids of the candy significantly as well as making it easier to mix into the fondant and creams. Dark colors are difficult to achieve with the whiteness of the crystalline material. When dyes are used, any migration or change in moisture can cause mottling. Many exempt "Natural" colors tend to function as dyes so the cautions apply to them as well. Caramel colors used at moderate to high levels can impart additional stickiness and should be used with care. Slight changes in base formulation can sometimes counteract higher liquid caramel levels.

Other ingredients that are normally added for flavor can impart color as well. They are not classified as colors, but can help differentiate flavors. Freeze or roller dried fruit powders, cocoa/cacao mass, instant coffee, roasted nut pastes, and maple/brown sugar can all impart color to fondant and creams.

9.2.6 Frappé

Frappé, a whipped sugar foam, is a key component to a good cream since it lightens the texture of a dense fondant. Frappé is made by whipping sugars (glucose syrup and sometimes sucrose) together with a protein stabilizer (egg whites, soy proteins and/or gelatin) to make an aerated product similar to marshmallow (see Chapter 11). Typically, frappé is aerated until it becomes a thick foam, with a density between 0.35 and 0.5. A good frappé has numerous small air cells held firmly by the protein to retain air when it is blended into the fondant. The air bubbles in frappé also provide a whiter, more opaque characteristic to the cream.

9.2.7 Fats

In some creams, particularly butter creams, it is desirable to have a small amount of fat, perhaps up to 7–8% of the total product weight. The fat provides lubricity in the mouth and a specific flavor release associated with lipid-based flavors. In buttercreams, real butter is most often desired for the natural flavor; however, hardened vegetable fats are often used with appropriate flavorings to reduce costs.

Since lipids reduce aeration and whipping efficiency, any fats or lipid-based flavors must be added carefully at the end of the process so as to minimize deaeration of the frappé.

9.2.8 Preservatives

No microbial growth will occur in fondants and creams if they are formulated correctly, with water activity of the liquid phase below about 0.65. At times, chemical preservatives like sorbic acid or potassium sorbate may be added to inhibit mold growth when the water activity is higher.

9.2.9 Invertase

The enzyme invertase is often added to fondants and creams to provide a softening effect during storage. Incorporating invertase into a fondant or cream formulation converts an initially hard product, one that can be enrobed or panned, into a softer product during storage. The level of invertase added (0.1–0.3%), the water content of the cream, and the nature of the sweetener phase determines the ultimate end point of softening. More details about invertase activity are given in Section 9.4.2. The action of invertase causes a decrease in water activity, thereby extending shelf life.

9.3 Manufacturing

The manufacturing steps for making fondants and creams depend on the size of the operation and the nature of the product being made. Fondants and creams can be made either in small batches or in high-capacity continuous processes. Fondants and creams also can be made either by crystallizing the sugars within the batch or by adding water to a powdered fondant sugar. The general steps in production of fondant by the crystallization process are shown in Figure 9.1.

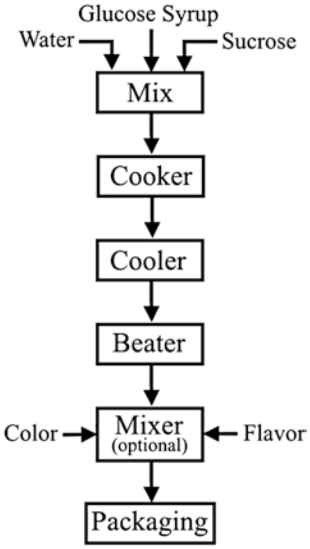

Figure 9.1 Typical process schematic for making fondant

Small candy makers generally make fondants and creams in batch cookers. The sugar and water are weighed out and heated in a kettle, and once the sugar is completely dissolved, the glucose syrup is added. Heating continues as the batch begins to boil and temperature increases. Once the desired boiling point temperature (indicative of the final water content) is reached, the batch is carefully poured into a mixing vessel (like a cream beater) and allowed to cool undisturbed. After cooling to the appropriate beating temperature, the mixer is turned on and crystallization is induced by the agitation of the beater. For cast creams, thinning syrup, colors, flavors and frappé are added, as desired, to the fondant, the mixture is warmed carefully to reach the desired fluidity for depositing, and the fluid mixture is deposited into molds (starch or starchless) for cooling and solidification.

Large candy makers use a continuous process for making fondant and cream. Liquid sugar (67% solids) and glucose syrup are mixed and immediately cooked to the desired temperature (water content). The cooked mass is cooled statically (no agitation) to the proper beating temperature (for example, on a cooling wheel), at which point intense agitation is applied to generate massive nucleation of sugar crystals. Additional ingredients like colors, flavors and frappé may be added at this point, usually in-line, while the fondant is still warm and somewhat fluid. If the fondant is to be stored for later use, it is collected and cooled. If the fondant is to be used immediately for making creams, it is sent for appropriate subsequent processing to create the final product.

9.3.1 Fondant

Producing fondant by crystallization requires several steps: (1) preparation of a sugar syrup, (2) concentrating that syrup to the appropriate water content, (3) cooling it to the desired beating temperature, and (4) massive agitation to crystallize the fondant. The resulting product has semi-solid characteristics dependent on the nature of sweeteners used and the final water content. Figure 9.2 documents how the steps in the fondant-making process are visualized on the state diagram (see Section 2.10).

9.3.1.1 Syrup Preparation and Concentration

The essential ingredients in the starting formulation for many fondants are sugar, glucose syrup and water. Sufficient water (typically 20% of batch weight) is added to completely dissolve the granulated sugar. Since excess water added at this point has to be boiled off, only the minimal amount of water needed to dissolve the sugar should be added. To ensure that all sugar crystals are dissolved prior to cooking, some manufacturers add the glucose syrup after all the granulated sugar has been dissolved. Sometimes, a pressure dissolver can be used to reduce the amount of water needed and to speed up the syrup preparation step. Dissolution in a pressure dissolver is faster than in atmospheric dissolution because the water is retained in liquid form at higher temperatures to promote dissolution.

The sugar syrup is then cooked to the specified temperature to give the desired water content. The relationship between boiling temperature and water content is given for the specific mix composition (sugar and glucose syrup). Cook temperature may be compensated for fluctuations in atmospheric temperature to ensure the correct water content is attained (see Section 2.7 for further details). Normal atmospheric pressure fluctuations can lead to as much as half a percent difference in water content from the highest high pressures to the lowest low pressures. Cook temperatures must also be adjusted for manufacturing at higher elevations.

To promote rapid evaporation of water from the syrup and to quickly reach boiling point temperature, the choice of cooking unit is critical.

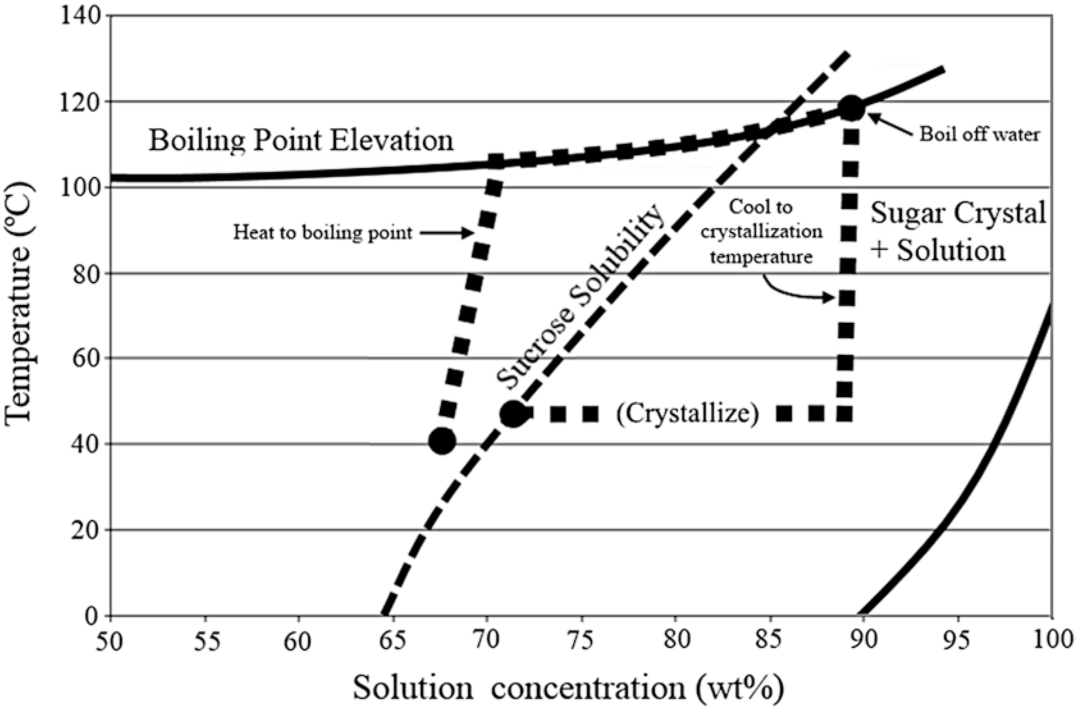

Figure 9.2 Sequence of process steps in fondant making depicted on the state diagram for a mixture of 90% sucrose and 10% 42 DE glucose syrup solids (With permission from Hartel et al. 2011)

If heating is slow, crystallization can potentially occur during cooking when the boiling point curve exceeds the solubility curve (see Section 2.9.1). Batch cooking must be sufficiently fast and the formulation must contain sufficient glucose syrup to avoid crystallization. When cooking a small batch of fondant, a candy manufacturer often uses a wet brush to wipe down the surface of the kettle where boiling is taking place since this is the most likely spot for grain formation. Even though the small amount of water added during this wiping action must be boiled off again, the extra water is critical to redissolve any crystals that form in the kettle prior to cooling and beating.

In continuous operations, rapid evaporation methods, with high rates of heat and mass transfer, are used for cooking fondant syrups. The concentration of sugar syrups from 70% to 75% dissolved solids to 88–90% dissolved solids can be accomplished in a minute or two. Thin-film evaporators (microfilm cookers) are common for this purpose, as are shell and tube heaters. In a shell and tube heat exchanger, the syrup under pressure flows through a bundle of tubes housed inside a steam chest. Because of the elevated pressure inside the tube bundle, the water in the sugar syrup remains liquid even at temperatures of 115–121 °C (240–250 °F). After reaching the desired temperature, the syrup enters a flash chamber where pressure is reduced suddenly and the water flashes off as steam. The concentrated syrup is collected at the bottom of the flash chamber.

9.3.1.2 Cooling and Crystallization

Once the sugar syrup has reached the desired moisture content, it must be rapidly yet gently cooled to a temperature where optimal crystallization occurs. If crystallization takes place during cooling, the crystals formed grow significantly larger than those that are formed later in the beating stage. Thus, it is critical that the hot syrup be cooled quickly and without agitation to prevent undesired spontaneous nucleation of the supersaturated syrup.

Numerous methods have been developed to cool the supersaturated sugar syrup quickly.

Figure 9.3 Cream beater (Courtesy of Savage Bros.)

Probably the simplest cooling method is to pour the hot liquid onto a cold table or surface. For hand beating of fondant, a cold table with controlled temperature (via water circulation) would be used.

In small-scale operations, fondant is still made in batches on a cream beater (Figure 9.3). The hot fondant sugar syrup is poured onto a flat circular platform cooled from below with circulating water. When the sugar syrup cools to the optimal beating temperature, the beater motor is engaged, which causes a series of plows to rotate, scraping the syrup off the platform and distributing it around and behind the plows. This agitation is sufficient to induce crystallization over a period of 20–30 min. Since this process is generally open to the surrounding air, crystallization on a cream beater often leads to a slight loss of water (1–2%) to the environment. This water loss must be offset by cooking to a lower temperature to give a slightly higher initial water content.

A common cooling technology for larger-scale operations is a refrigerated cooling drum. The syrup is applied in a relatively thin (5 mm) layer to the top of a slowly turning drum with refrigerated water circulating within the drum to provide cooling (Figure 9.4). The drum turns slowly (about 1 RPM) to allow adequate time for the syrup mass to cool sufficiently before it is scraped off. Near the bottom of the drum, a scraper blade removes the cooled amorphous

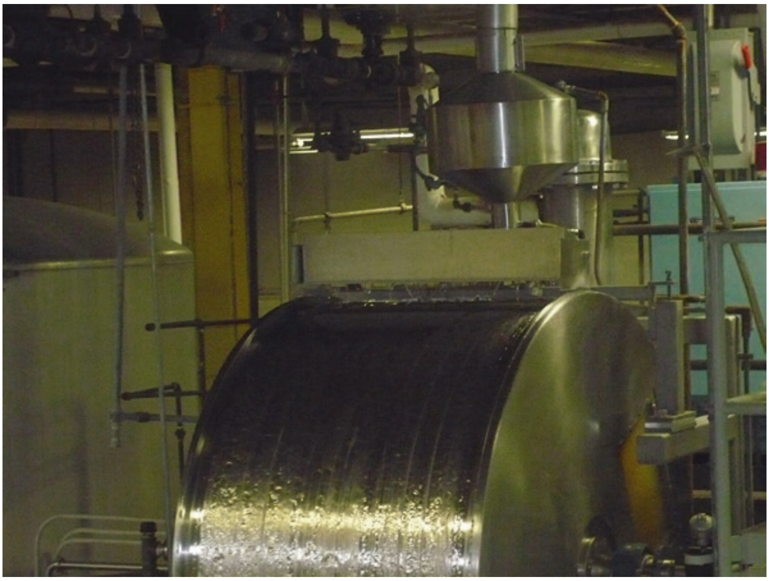

Figure 9.4 Cooling drum for fondant showing syrup distributor at the top of the drum (Courtesy of Lawrence Foods)

syrup and deposits it into the hopper that feeds the beating tube. The amount of syrup loaded onto the drum and the RPM of the drum are matched to the desired production capacity so that the syrup entering the beating tube has cooled to the proper temperature by the time it reaches the scraper blade. In order to ensure that no crystals are formed on the cooling drum after the cooled layer is scraped off, the surface of the drum at this point is cleaned with a spray of steam. This ensures that fresh cooked syrup applied at the top of the drum rotation falls onto clean (without crystals) metal surface. Without this cleaning step, a crystallized layer would eventually form on the drum surface, seeding the supersaturated sugar syrup and leading to uncontrolled crystallization.

Once the syrup has cooled to about 45–50 °C (114–122 °F), it is ready for intense agitation to promote spontaneous crystallization. At this temperature, the sugar mass is at the optimal supersaturation to promote the maximal rate and extent of crystallization (see Section 2.11.2). Intense mixing at this point is desired to promote formation of numerous small sugar crystals that give the desired smooth texture. If temperature is too high in the beating stage, the lower supersaturation means fewer crystals are formed. Likewise, if temperature is too low in the beating stage, the viscosity is too high and again fewer crystals are formed. In both cases, the end result is larger mean crystal size and coarser fondant. It is critical that the beating temperature be kept at the optimal point to ensure the finest sugar crystals and smoothest fondant.

Continuous fondant beaters are typically cylindrical-shaped mixers with blades that turn on a central shaft with stationary pins to provide intense shearing (Figure 9.5a). The agitation rate of the beaters is about 100 RPM, with a residence time of about 6 min in the beating tube. Clear syrup enters one end of the beating tube (Figure 9.5b) and fully crystallized fondant exits. The massive crystallization that takes place in the fondant beater tube relieves the supersaturation of the sugar syrup almost instantaneously, meaning that billions of crystals are formed in a very short time period. Because so many crystals are formed, they all remain quite small since there is only a certain amount of crystalline mass to spread among the myriad crystals. The massive crystallization also causes a temperature increase of a few degrees due to the release of latent heat. To offset this heat input due to crystallization, cooling water is usually circulated through the jacket of the beater tube to maintain desired temperature.

The product exiting the beating tube is still somewhat fluid so it can be pumped. This is in

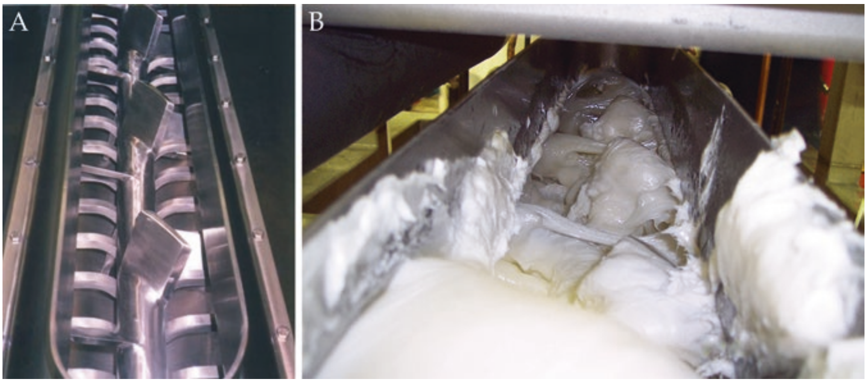

Figure 9.5 Opened continuous fondant beating tube: (**a**) empty tube, (**b**) stop flow during operation showing progression of fondant graining from *top* to *bottom* (Courtesy of R. Hohberger, SPEC Engineering)

part because it is still warm, but also because crystallization has not been quite completed yet by the time it exits the beating tube. Thus, it retains some fluidity despite the large amount of crystalline material. From here, fondant either goes to packaging for later use or undergoes further processing steps (i.e., ingredient addition, cream production, etc.).

9.3.1.3 Packaging

Since fondant is often used as an ingredient in other manufacturing processes (i.e., creams, icing, frosting, etc.), it can be collected and stored for later use. Typically, pails or boxes are filled with fluid fondant as it exits the mixer, which are then allowed to cool as the fondant continues to crystallize for subsequent storage and distribution. Cubes of fondant weighing 22.7 kg (50 lb) are common for distribution.

9.3.1.4 Ingredient Addition

If the fondant exiting the beating tube is to be used directly, usually additional ingredients need to be added. Since the fondant is still sufficiently fluid as it exits the beating tube, this provides an ideal point for addition of other ingredients. Colors, flavors and frappé (for creams) may be added into the fluid fondant by mixing in a second beating cylinder (Figure 9.1). The agitation in this mixer (50–60 RPM) is not as intense as in the fondant beating tube, but is sufficient to completely incorporate these other ingredients within the residence time (≈6 min) so that the product exiting the second tube is completely mixed. This product may be packed and stored for later distribution or may be pumped directly to the next stage for processing.

9.3.2 Powdered Fondant

Dried fondant sugar (or icing sugar) is also produced for certain applications, particularly for icings and extruded cream pastes. Fondant sugar is usually produced by micropulverization. Refined sugar is ground with 2.5–10% glucose syrup solids, maltodextrins or other low DE (dextrose equivalent) cereal products as a flow aid to help improve flowability of the powder, to control moisture, and provide enhanced dispersion in water. In the ground powder, 99% of the particles are less than 44 μm in size (pass through a US Number 325 mesh sieve). Powdered fondant can also be made by crystallization in an extruder, followed by grinding and sieving.

9.3.3 Creams

Fondants are typically used as the starting point for making creams. Deposited, or cast, creams are made by melting fondant in a bob syrup prior to depositing into a mold, whereas extruded creams are typically made by forming a paste from fondant sugar powder. Many cream candies are coated in chocolate after solidification, either by shell molding (see Section 15.6.1), enrobing through a curtain of chocolate (see Section 15.6.2) or by a panning process where a chocolate shell is applied by sequential applications of liquid chocolate (see Chapter 17).

9.3.3.1 Deposited (Cast) Cream

The general process for making cast creams is shown in Figure 9.6. To prepare a cast cream, fondant is diluted with thinning syrup and frappé is added to provide a lighter texture. A typical formulation for deposited cream is given in Table 9.2. A typical cream has about 40–45% fondant, 10–25% frappé and 34–38% thinning syrup, depending on the desired fluidity and hardness of the cream product. Colors and flavors are added to suit the product needs. The semi-fluid product is then deposited into molds to form the final shapes, which are cooled and allowed to set prior to subsequent use (e.g., chocolate enrobing).

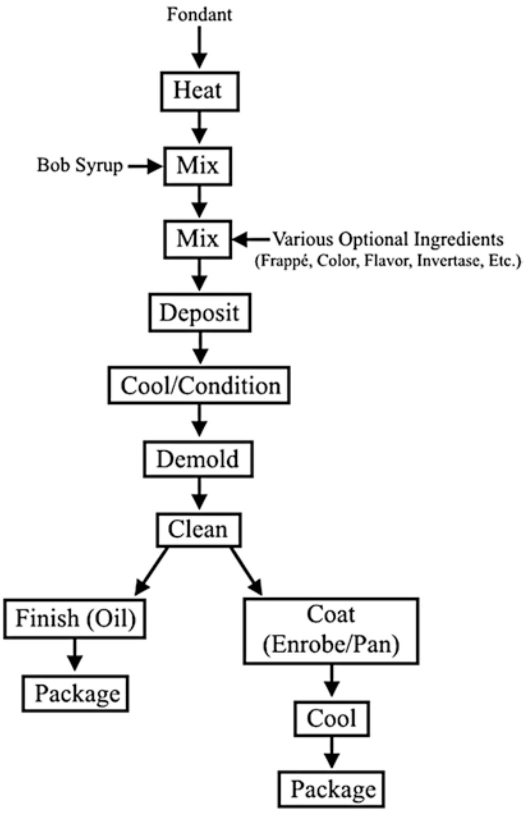

Figure 9.6 Typical process schematic for making deposited cream

Frappé is made by whipping glucose syrup (sometimes with sucrose) in the presence of a protein stabilizer (egg albumen, gelatin, etc.) to a specific gravity of between 0.3 and 0.4. Whipping frappé is accomplished in a high-speed whisk, either at atmospheric pressure or at elevated pressures. In a pressurized whisk, a specified amount of air is incorporated into a known amount of syrup to produce a frappé with specific density. Either air or an inert gas like nitrogen can be whipped in a pressure whisk.

Thinning syrup (sometimes called “bob” syrup) is made of dissolved sucrose, glucose syrup and sometimes invert sugar. A typical composition of thinning syrup is about 3 parts granulated sucrose, 1.6 parts glucose syrup (usually 42 DE) and perhaps 0.8 parts invert sugar, cooked to about 117 °C (242 °F) to reduce water content to about 11 or 12%. Ideally, addition of thinning syrup does not cause dissolution of any of the small crystals in fondant, it just dilutes the crystals by adding a syrup with the same composition (sucrose, glucose syrup solids and water content) as the liquid phase of the fondant. This disperses the crystals in the fondant and provides sufficient fluidity to allow molding. In principle, the composition of the thinning syrup should match the saccharide composition of the continuous phase of the fondant. However, since the thinning syrup is warm, some of the sugar crystals in the original fondant are dissolved due to the higher solubility at the higher temperature (see Section 2.8). Thus, the process of adding thinning syrup is often called remelting (although technically it probably should be called redissolving). The result of adding warm thinning syrup to prepared fondant is to thin out the fondant so that it can be used for forming and molding. The reduced viscosity, due to warmer temperatures, reduced crystalline sugar content and increased liquid phase, allows the fondant to be poured into molds and formed into desired shapes.

Even when the thinning process is done carefully, the sugar crystals in the finished cream do not return to exactly the same state (number and size) of the original fondant upon cooling. When the thinned fondant cream is cooled, additional sugar crystallizes out of the solution onto the remaining sugar crystals. Crystallization continues until phase equilibrium is attained, meaning the sugar molecules in the solution (liquid) phase have reached equilibrium with the sugar molecules in the crystalline (solid) state. However, since some of the original sugar crystals in the prepared fondant were dissolved away, there are fewer crystals in the remelted fondant and when cooled to the same temperature, each of the remaining crystals must grow a little larger to accommodate the recrystallized mass. Thus, remelted fondant typically has a slightly larger mean size than the original fondant, which may result in the cream being perceived as slightly coarse. Great care is needed when remelting fondant to make deposited creams – the lowest temperatures that still give the desired fluidity are recommended. Temperatures above about 80–82 °C (175–180 °F) are not recommended.

The fluid creams made by thinning fondant and adding frappé are deposited into molds and allowed to set into the desired form. Depositing of fondant and cream candies is done in either candy-shaped depressions formed in molding starch (starch mogul) or in pre-shaped plastic molds (starchless molding).

9.3.3.1.1 Starch Molding

In starch molding of cast creams, the thinned liquid cream is deposited into impressions in a tray of dry powdered starch (usually corn starch) and allowed to solidify. Imprints of the desired shape are pressed into a layer of starch prepared in a starch board. The starch is usually treated with a small amount of oil (mineral or vegetable) to help shape retention and reduce dusting. Water content of the starch should be within 5–7% in order to provide proper drying of the cream during curing. The liquid cream is deposited through a nozzle to fill the imprints in each board. The temperature and water content of the deposited cream must be carefully controlled so that the viscosity of the fluid cream is sufficiently low that it completely flows into all details of the impression to give the desired shape. Temperatures of 65–71 °C (150–160 °F) are common for the depositing cream. Typically, the water content of the fluid cream being deposited is 1 or 2% higher than the final desired water content of the cast cream since the cream loses water to the starch during curing.

Filled trays are held, or cured, overnight to allow the creams to solidify and lose moisture. Curing takes between 3 and 24 h at temperatures of 24–27 °C (75–80 °F) and 50–60% RH. After solidification, the starch trays are upended and the candy pieces separated from starch on a screen. The separated candies remaining on the screen proceed to the next step in the operation, while the starch, which passes through the screen, is dried and reused in the starch mogul.

Some deposited cream candies, such as candy corn, require sequential depositing steps to build the different colored layers. In candy corn, three sequential cream deposits, first the white, next the orange, and finally the yellow, are deposited into a corn kernel shaped mold. Timing of each deposit is critical to ensure that each of the three layers adheres properly to the other layers.

Additional details of starch depositing and starch mogul operation can be found in Section 12.3.2.2.1.

9.3.3.1.2 Starchless Molding

Because starch molding is time consuming and creates a hazardous, dusty environment in the plant, cast creams may often be deposited into molds made of rubber (or some other flexible material). The main advantage of starchless molding is that process times can be shortened considerably, compared to starch molding, by elimination of the curing step. However, some differences in formulation are usually necessary since there is no moisture loss during setting.

Solidification of cast creams in rubber molds occurs solely by cooling, rather than by a combination of cooling and drying. Therefore, the liquid cream must be close to the final desired water content when it is deposited. The lower water content for creams cast in rubber molds means that the viscosity of the fluid cream is higher than the viscosity usually used for molding into starch. The higher viscosity may limit certain applications where intricate designs are required. However, the main disadvantage of starchless molding is the lack of flexibility to change shapes since it can be quite time consuming to change molds in the depositing machine. Typically, starchless molding is most useful for large quantity production runs of a single product shape.

In starchless molding, solidification times are generally short enough that cooling tunnels can be used to set the creams. Often, a continuous conveyor operation is used. Empty molds enter the depositing section and are filled with liquid cream. The filled molds exit the depositing section and immediately enter the cooling tunnel, where conditions of temperature and airflow are matched with the residence time in the tunnel (20–30 min) such that the creams have solidified sufficiently upon exit from the tunnel. Within the tunnel, the creams cool, solidify and shrink slightly as sugar crystallization occurs. The molds are turned upside down to remove the candy creams, sometimes assisted by stretching the molds to apply torque to help the creams come out. If necessary, the molds are cleaned before they re-enter the depositing section of the machine for another round of depositing candies. In general, starchless molding requires moisture contents of 12% or less. Higher moisture content causes the cream centers to stick to the mold and cause problems with operation.

9.3.3.1.3 Chocolate Molding

To make cream-filled chocolate, either hollow-shell molding (see Section 15.6.1) or single-shot depositing (see Section 15.6.1) are most often used. In hollow-shell molding, tempered chocolate is deposited into a mold, the mold is over-turned and liquid chocolate shaken out, leaving a shell of chocolate lining the mold shape. After cooling to solidify the chocolate, cooled cream is deposited into the mold, taking care not to overfill the form. The temperature of the cream must be sufficiently low that the chocolate shell is not melted. A layer of tempered chocolate is then applied to the top of the cream-filled mold and the excess chocolate scraped off. The chocolate bottom fuses with the chocolate shell to provide a complete encasing of the cream. After cooling, the molds are over-turned to release the cream-filled chocolates for subsequent packaging.

Fondants and creams may also be deposited into molds along with a chocolate coating in single-shot depositing technology. Here, dual nozzles are used with chocolate applied through the outer nozzle and cream paste applied through the inner nozzle (see Section 15.4.11.1). Pump actuators are carefully synchronized to initiate the chocolate flow into the mold an instant before the center cream filling is initiated. This allows a chocolate layer to form first along the mold surface. The cream paste pump is stopped an instant before the chocolate pump is stopped to allow a complete chocolate coating surrounding the cream paste. When done correctly, the entire operation of depositing a chocolate-coated cream center piece can be done in a single step. It is imperative that viscosities of both cream center and chocolate exterior are carefully controlled for proper single-shot operation. Temperature, water content and crystalline content of the cream paste are critical parameters that must be controlled to attain the desired viscosity. If not properly synchronized, uneven chocolate coatings can be formed. In extreme cases, improperly sealed pieces can be formed that subsequently leak filling.

9.3.3.2 Extruded Cream

An extruded cream piece can be made by mixing powdered fondant with sufficient water to make a paste (with a dough-like consistency) and then forming the pieces by extruding the paste through specially-designed nozzles or dies. A typical process for making extruded creams is shown schematically in Figure 9.7. A typical formulation for an extruded cream is given in Table 9.3.

The principle ingredients are powdered fondant, or icing sugar, and water. When water is added to the powdered fondant sugar, some of the sucrose crystals dissolve until the water becomes saturated with sucrose. At this point, the physical properties of the mixture depend on the relative level of water added to the dry fondant powder. At about 8–10% water, the mixture takes on the consistency of a very firm paste. With more water added, more sugar crystals dissolve and the fondant becomes thinner and may even flow. Generally, conditions that give a pliable paste or dough are desired since this consistency can be

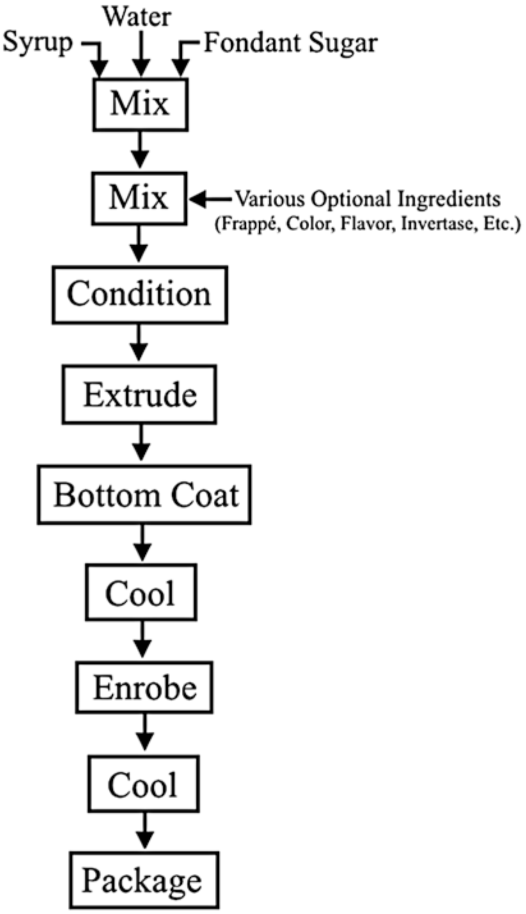

Figure 9.7 Typical process schematic for making extruded cream

easily extruded and formed into the desired shape, but still sufficiently firm to maintain its shape for subsequent processing.

Other ingredients that may be added to enhance extruded creams include melted butter or vegetable fat (4–8%) to make a buttercream, colors and flavors to suit, and the enzyme invertase (0.1–0.3%) to promote softening during storage (see Section 9.4.2).

Once the paste is made, individual pieces are often formed by extrusion. In the extrusion process, the paste is forced through a die with the desired shape and cut into individual pieces by a knife or wire passing across the die face. Alternatively, the creams can be deposited directly onto a belt into the desired shape. The individual pieces are collected on a conveyor, cooled to solidify the piece, and taken for further processing (usually enrobing in chocolate). Alternatively, creams can be deposited directly onto a chocolate wafer, as seen in Figure 9.8, which eliminates the need to pre-bottom the cream before enrobing.

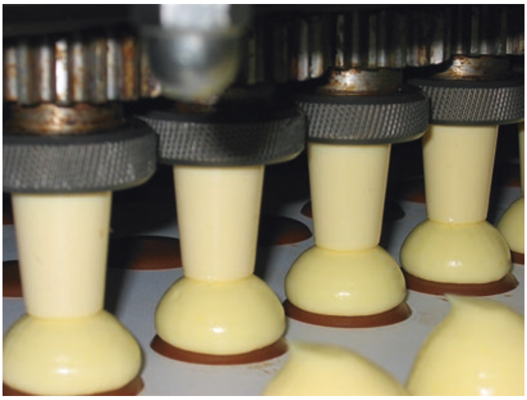

Figure 9.8 Depositing cream onto a chocolate wafer (Courtesy of Hacos)

9.4 Product Characteristics

Many factors affect the quality of fondants and creams, but none are more critical perhaps than the nature of the sugar crystals. The amount of crystalline material and the size distribution of the crystals govern texture (hardness, flow characteristics, etc.), flavor release, shelf life, and sensory evaluation of smoothness. Thus, control of particle size is one of the most critical control points in fondant production.

The liquid phase also plays an important role in texture and shelf life of fondants and creams, particularly governing water activity and specifically, the ability to support microbial growth. Since a large portion of the sugar is in crystalline form, the dissolved solids concentration of the liquid phase is low (relative to ungrained confections), and this can lead to a sufficiently high water activity to support mold growth. Thus, certain additives, like corn syrups and other humectants, are important additions to the formulation to control water activity (and texture). The use of invertase in creams provides an additional level of control of texture and quality.

9.4.1 Microstructure and Product Properties

Fondant is a highly crystallized dispersion, with numerous, small sugar crystals distributed within a liquid matrix. A cream is similar in structure, although it also contains small air bubbles from the addition of frappé. The relative ratio of crystalline phase to liquid phase, the nature of the crystalline dispersion, and the composition of the liquid phase are important factors governing the texture, quality and shelf life of fondants and creams.

Numerous factors influence the rate and extent of crystallization during manufacture of fondant (Lees 1965; Hartel 2001).

- Supersaturation: The driving force for crystallization, supersaturation, is a function of syrup concentration, composition and temperature (see Section 2.10). Higher supersaturation promotes more rapid crystallization, up to the point where molecular mobility is impeded as viscosity increases.
- Beating temperature: As seen in Figure 9.1, the sugar mass must be cooled to the temperature at which nucleation rate is highest to generate the largest number of crystals.
- Beating intensity: Crystallization is enhanced by rapid and intense agitation.
- Presence of crystallization inhibitors: Various ingredients added to fondant (e.g., invert sugar, glucose syrup, etc.) are known to inhibit crystallization rate and decrease the crystalline phase volume in fondant. In part, this effect comes from a combination of specific inhibition of crystallization and modification of the phase diagram (see Section 2.8).

In turn, the crystallization process determines the nature of the crystalline phase, which then affects the texture and sensory properties of the fondant.

- Crystal size distribution: In a smooth, creamy fondant, crystal sizes range from as small as a micron or so to 15 μm. Mean crystal size should remain below 15 μm with only a few crystals above 20 μm.
- Crystal content: Arguably, the most important determinant of fondant texture is the amount of crystalline material, or rather, the ratio of crystalline to liquid phases. As crystal content increases, hardness of fondant increases accordingly.
- Liquid phase: As crystal content goes up, the liquid phase decreases proportionally. Beyond the amount of liquid phase, its composition also has significant influence on fondant quality. In particular, water activity of the liquid phase governs the water activity of the fondant (crystals do not contribute to water activity, so in principle the water activity of the liquid phase is what is measured for fondant).

Although many of these topics have been mentioned in previous sections, the principles that govern these effects are discussed here in more detail.

9.4.1.1 Crystalline and Liquid Phases

In a normal fondant, somewhere between 45% and 60% of the mass is made up of very small sugar crystals, with the rest of the mass in the liquid phase. The exact amount of crystalline sugar is important because higher crystal content leads to a firmer fondant (and vice versa). The liquid phase of fondant contains all the water in the fondant (no water is contained within the sugar crystals) plus dissolved sugars (sucrose, glucose syrup, invert sugar, etc.). Phase equilibration in fondant, which may take several days to achieve, means that the maximum amount of crystals is produced and the solution phase concentration is at the saturation concentration at storage temperature. Thermodynamically, phase equilibrium means that the sucrose molecules in the crystals have the same chemical potential as the sucrose molecules dissolved in the aqueous phase. Since the two phases are at equilibrium, the amount of crystalline sugar present in the fondant (or crystalline yield) can be calculated from a mass balance based on the starting concentration of sucrose and the final solubility of sucrose in the solution, which depends on the temperature and the effects of any other additives, like corn syrup or invert sugar.

Fondant gets its solid-like characteristics, to a large extent, from the high crystalline phase volume. That is, the number of sugar crystals and the distribution of their sizes have a major impact on the physical properties of the fondant. The relative distribution of crystalline to liquid phases is the main factor influencing the physical properties of fondant. In general, the higher the ratio of solid to liquid (crystalline phase volume), the firmer (harder, denser, etc.) is the fondant. Formulations with high levels of sucrose (lower corn syrup) and low water contents lead to hard fondants because of the increased sugar crystal phase volume. Formulations with higher levels of glucose syrup (or invert sugar) and cooked to lower temperatures (higher water content) give softer fondants.

The liquid phase contains all of the water in the fondant as well as dissolved sugars. Any glucose syrup, invert sugar or other dissolved components (e.g., humectants) added to the formulation are found in the liquid phase along with whatever sucrose remains dissolved. The amount of sucrose dissolved in the liquid phase of fondant depends on what other sugars are present in the formulation since sucrose solubility concentration is influenced by the other sugars in the formulation (see Section 2.8).

The water activity of fondant, as measured by the relative water vapor pressure above the fondant, is determined by the liquid phase composition. That is, the crystals in fondant have no effect on water activity of the fondant since they do not contribute to the relative vapor pressure. If a fondant was made with pure sucrose, the concentration of the liquid phase would be 67%, the solubility concentration of sucrose at room temperature. This is true regardless of the final water content of the fondant (see the mass balance equations in Appendix A.9.1). The water activity of a 67% sucrose solution is approximately 0.85 (Norrish 1967), a value where the fondant would be prone to microbial growth. One of the functions of glucose syrup, besides moderating texture of the fondant through control of crystal content, is to decrease the water activity. In the example in Appendix A.9.1 for fondant with 12% water and 70/30 sucrose to 42 DE glucose syrup ratio, the total dissolved concentration in the liquid phase was calculated to be 78%. This is well above the 67% concentration for pure sucrose because the entire amount of glucose syrup solids can be found in the liquid phase. The glucose syrup solids raise the concentration, and also lower the water activity of the liquid phase. In the example in Appendix A.9.1, the water activity of the fondant is approximately 0.78 (based on the Norrish correlation; see Section 3.3.2).

Even with 30% glucose syrup, the water activity of fondant is still considerably above the threshold water activity value at which no microbial growth can occur (0.65). To reduce water activity of fondant even further, additional sugars and humectants can be added, including invert sugar and glycerol. These humectants also impact texture by reducing the amount of crystalline solids, but have a significant effect on reducing water activity since they are small molecular weight sugars.

The nature of the dispersion of the crystalline phase is also critical to the texture and consumer perception of fondant. Figure 9.9 shows a microscope image of typical sugar crystals observed in fondant cream candy. It has been estimated that there are approximately 3.6×10^{11} crystals in every 100 g of fondant mass (Lees 1965). This very large number of crystals with small average size gives fondant its characteristic properties. From a sensory standpoint, the mean size of sugar crystals in fondant should be less

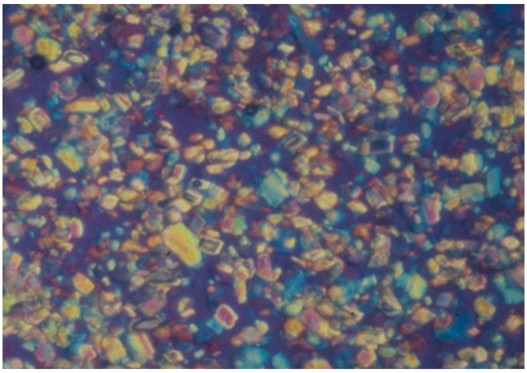

Figure 9.9 Sugar crystals in fondant observed by transmission optical microscopy with crossed polarizing lenses. Magnification 40×

than about 10–12 µm. The threshold detection size, or the smallest size that can typically be detected by a consumer, for sugar crystals in fondant is somewhere around 15–20 µm. Crystals much larger than about 20 µm are easily detected by the consumer and impart a coarse texture to the fondant.

Sugar crystal size in fondant can be quantified with any of several different measurement methods, with image analysis of microscope images and laser light scattering being the two most common. Microscope images can be prepared by dispersing the fondant in an organic solvent (e.g., alcohol) that has previously been saturated with sucrose to prevent dissolution. The size distribution of the crystals can be quantified by image analysis of the images. This is a relatively simple method although depending on the resolution of the microscope, very small crystals (less than 1–2 µm) are difficult to quantify. The second method for particle size characterization in fondant is laser light scattering. Here, a dilute dispersion of the fondant in solvent is exposed to laser light and the extinction pattern of the scattered light observed. The size distribution is then calculated from the extinction curve based on light scattering theories. The two methods give slightly different results since they measure different aspects of the crystal dispersion. Microscopy/image analysis measures the projected area of the crystals as they are dispersed on the microscope slide, whereas light scattering measures the volume of particle that scatters the laser light. Furthermore, crystal size can be stated based either on a population basis or a volume (mass) basis, with the two methods giving very different results (see Hartel 2001 for more details). A population-based mean size puts more emphasis on smaller particles, which may be important when there are many more small crystals than large ones. A volume-based mean size, on the other hand, emphasizes the larger particles that carry the larger mass. This may be important when considering the sensory aspects of fondant since only a relatively small number of large particles may be sufficient to cause the fondant to be considered coarse to the consumer. For these reasons, it is important to exercise caution when describing crystal size distributions and to clearly specify which averaging method was used.

To produce the numerous small crystals found in fondant, it is extremely critical to control crystallization. In particular, the nucleation rate (rate of formation of crystals, #/mL-second) must be extremely high in the beating tube. Formulation and processing conditions must be controlled to ensure this rapid rate of nuclei formation to ensure that all crystals remain below the critical threshold detection size.

9.4.1.2 Parameters That Affect Microstructure

Both thermodynamic and kinetic parameters affect microstructure in fondant. The thermodynamically-governed microstructural characteristics include crystal content, liquid phase content, and liquid phase composition. For a given formulation, these parameters will be the same regardless of the processing conditions, assuming that the system reaches a phase equilibrium (a good assumption for commercial fondant processes).

The primary kinetically-governed characteristic is the sugar crystal size distribution since the span of crystal sizes is controlled by the relative rates of nucleation and growth and the time span over which nucleation occurs (Hartel 2001). Both formulation and processing conditions affect crystal size distribution by influencing crystallization rates.

9.4.1.2.1 Formulation Effects

Water content in fondant, which typically varies from approximately 8 to as high as 15%, can cause significant differences in physical properties. Fondant with low water content is very solid, to the point of being hard and even brittle, whereas fondant with high water content is soft and runny. These differences are related primarily to the amount of crystalline phase, which imparts the solid-like characteristics. With high water content, more of the sucrose is dissolved in the solution phase so there is less crystalline mass. Although the syrup phase has higher dissolved solids concentration, the lower crystal content results in a softer and runnier fondant.

The opposite is true for fondant with low water content. In this case, less water means more of the sucrose is in crystalline form, so the fondant is harder and more solid-like. Table 9.4 shows the effects of water content on crystal content, liquid phase content and liquid phase concentration in fondant equilibrated at room temperature. These are calculated values from the approach detailed in Appendix 9.1.

Glucose syrup content in fondant may vary from as low as 5% to as high as perhaps 30%. When sucrose is replaced by glucose syrup in a fondant formulation, there is less sucrose to crystallize and the crystal content is reduced. However, glucose syrup also affects the solubility concentration of sucrose in water, so the net effect is complex. When higher glucose syrup levels are used, the crystal content in the fondant is decreased but since all the glucose syrup remains in the solution phase, the final dissolved solids concentration of the liquid phase is increased (Table 9.4). This effect, where the mixture of sucrose and glucose syrup at saturation has a higher total solids content than sucrose at saturation, is discussed in more detail in Section 2.8.

Glucose syrup has also been shown to affect crystallization rates of sucrose, with levels over 20–30% glucose syrup significantly decreasing nucleation and growth rates (Hartel 2001). Thus,

Table 9.4 Effects of sucrose to glucose syrup (42 DE) ratio (on a solids basis) on crystal content, liquid phase content and liquid phase dissolved solids (calculated) of fondants at different water contents

Sucrose: glucose syrup	Water (%)	Crystal content (%)	Liquid (%)	Liquid concentration (%)	Water[a] activity
90/10	9	66.1	33.9	73.5	0.819
	10	63.0	37.0	72.9	0.821
	11	60.0	40.0	72.5	0.823
	12	57.0	43.0	72.1	0.825
	13	53.9	46.1	71.8	0.827
	14	50.9	49.1	71.5	0.829
	15	47.9	52.1	71.2	0.831
80/20	9	60.1	39.9	77.5	0.785
	10	57.1	42.9	76.7	0.792
	11	54.2	45.8	76.0	0.797
	12	51.2	48.8	75.4	0.802
	13	48.2	51.8	74.9	0.806
	14	45.2	54.8	74.4	0.810
	15	42.3	57.7	74.0	0.813
70/30	9	54.1	45.9	80.4	0.753
	10	51.2	48.8	79.5	0.763
	11	48.3	51.7	78.7	0.772
	12	45.4	54.6	78.0	0.779
	13	42.5	57.5	77.4	0.785
	14	39.6	60.4	76.8	0.790
	15	36.7	63.3	76.3	0.795
60/40	9	48.1	51.9	82.7	0.722
	10	45.3	54.7	81.7	0.736
	11	42.5	57.5	80.9	0.747
	12	39.6	60.4	80.1	0.756
	13	36.8	63.2	79.4	0.764
	14	33.9	66.1	78.8	0.771
	15	31.1	68.9	78.2	0.777

[a] Estimated from Norrish equation (Norrish 1966)

one would expect glucose syrup also to affect the crystal size distribution in fondant through its combined effects on crystallization rates, saturation concentration, and supersaturation. Table 9.5 compares the approximate sucrose crystal size distribution in fondants made with different glucose syrup levels (Lees 1965). Interestingly, the fondant made with higher glucose syrup actually contained the smaller sized sucrose crystals. Despite the effect of glucose syrup on reducing sucrose nucleation over this range, the higher addition of glucose syrup resulted in smaller crystals. This was most likely due to differences in the amount of crystal mass found in fondants with 10% or 25% glucose syrup. Although there were probably fewer sucrose crystals in the fondant made with 25% glucose syrup (although no data are available for crystal numbers in this study), those crystals ended up being smaller because the crystal content was about 10% lower with the higher glucose syrup level (compared to 10% glucose syrup).

Humectants, like invert sugar, glycerol and sorbitol, also affect crystal content, liquid concentration and crystal size distribution in much the same way as glucose syrup. A similar effect to that of glucose syrup is seen upon addition of invert sugar and glycerol, where there is less sucrose to crystallize. However, with invert sugar and glycerol, the water activity of the liquid phase is reduced considerably, even more than for glucose syrup, due to the presence of low molecular weight compounds. In the case of glycerol, the syrup phase now contains glycerol and less water, so there is also less dissolved sucrose.

9.4.1.2.2 Manufacturing Effects

The manufacturing of fondant has already been covered in Section 9.3; here, the focus will be on the specific effects of manufacturing on control of fondant microstructure. Proper control of processing conditions is necessary to ensure the smallest size distribution of crystals (Lees 1965). Although formulation factors (water content, glucose solids, other texture enhancers, etc.) can affect the amount of crystalline material, processing parameters only affect the nature of crystallization and thus, influence the distribution of crystal sizes. Specifically, the processing factors that can affect crystallization in fondant include the rate of cooking (boiling off water to reach the final water content), the rate of cooling of the concentrated syrup, the temperature of beating, and agitation rate during beating. Furthermore, if there are any crystals that remain from the dissolver or are formed during evaporation or cooling, prior to the beating tube, these crystals will grow significantly larger than those formed in the beating tube, potentially giving the fondant a coarse texture. Thus, control of processing factors is critical for production of the highest quality fondant with the smallest sugar crystals and smoothest sensory perception.

The rates of evaporation and cooling are important parameters for controlling crystallization in fondant. Once the concentrated syrup exceeds the saturation concentration and becomes supersaturated (see Section 2.8), it is prone to crystallization. To make the finest crystals, however, the entire mass must be cooled to the optimal beating temperature before any crystallization

Table 9.5 Effects of glucose syrup (42 DE) addition on crystal content and sucrose crystal size distributions in fondant with 10% moisture content (Data from Lees 1965)

Sucrose: glucose syrup	Beating temperature (°C)	Crystal[a] content (%)	0–10 μm[b]	10–20 μm[b]	20–30 μm[b]	>30 μm[b]
90/10	40	60.2	92.3	7.4	1.1	–
	55	54.9	89.1	9.7	1.1	1.1
	70	53.6	83.2	12.2	3.6	1.1
75/25	40	50.9	99.8	0.2	–	–
	55	50.1	96.2	3.5	0.3	–
	70	44.5	89.5	7.7	1.8	0.4

[a] Approximate distribution of particle sizes

[b] Crystal content measured at beating temperature

occurs. Thus, there is a critical period of time from when the syrup becomes supersaturated (during the evaporation step and during cooling) to when it enters the beating tube and is crystallized. On Figure 9.2, this period extends from the point where the boiling point elevation curve crosses the sucrose solubility curve to the point where the cooled, concentrated syrup enters the beating tube. This supersaturated syrup must be handled very delicately to prevent premature crystallization during this time period. The glucose syrup in the formulation provides some crystallization inhibition, but the supersaturated syrup must still be handled very gently, with minimum shearing and agitation, during cooling and transport to the beating tube. Thin-film evaporators and cooling drums satisfy the rapid heating and cooling requirement so that a completely uncrystallized, yet highly supersaturated syrup, is delivered to the beating tube.

One of the most critical control points in processing fondant is the temperature at which it is beaten to induce sugar crystallization. The goal in fondant manufacture is to make as many crystals as possible by promoting the highest nucleation rate. There is an optimal temperature range for supersaturated sucrose syrup that provides this maximum nucleation, where the greatest numbers of crystals are formed (see Section 2.11). Temperatures both higher and lower result in lower rates of nucleation. This optimal temperature point (or range of temperatures) occurs due to a balance between two effects. First, as temperature of the uncrystallized syrup is decreased, the supersaturation of the solution increases. Thus, temperature must be low to induce high nucleation rates and massive crystallization. However, when temperature is too low, nucleation rate decreases dramatically, despite the greater supersaturation, due to the limited mobility of the sucrose molecules. Although some say this inhibition is due to the increased viscosity at this low temperature, it is actually the inability of sucrose molecules to move that cause the low viscosity and thereby, reduces nucleation rate. The optimal beating temperature range for most fondants falls between 45 and 50 °C (114–122 °F), as seen in Figure 9.10, which depicts the induction time (time needed for nucleation to occur) when concentrated sugar syrup is cooled directly to the indicated temperature. The induction time (and inversely, the rate of nuclei formation) decreases as beating temperature decreases to a minimum in the range of about 45–50 °C, followed by an increase in the induction time at lower temperatures.

Agitation rate during beating (or intensity of beating) also affects the ultimate crystal size distribution (Lees 1965). It is widely recognized that energy input to a supersaturated solution can promote nucleation. Thus, the mechanical agitation during beating helps to promote the highest nucleation rate, leading to the smallest crystals and smoothest fondant. Insufficient agitation results in lower nucleation rate and ultimately, larger mean crystal size.

If any crystals are present in the cooked syrup, the final crystal size distribution will have a population of larger crystals since the ones that form first spend more time in supersaturated conditions and grow largest. Seed crystals may be present from a number of possible causes:

- Insufficient dissolution of crystals during fondant preparation,
- Cooking syrup too slowly,
- Cooling of cooked syrup too slowly,
- Insufficient cleaning of the cooling drum prior to syrup deposition, or.
- Uneven cooling of syrup.

Any crystals present in the syrup prior to beating have the opportunity to grow throughout the process and grow significantly larger than those formed in the beating tube. Thus, it is critical to ensure that all crystals are dissolved prior to cooking and that nucleation occurs only in the beating tube.

9.4.2 Invertase

The use of invertase to soften fondants and creams, a practice used widely in the industry, allows production of a piece that is sufficiently hard to withstand coating with chocolate by panning or

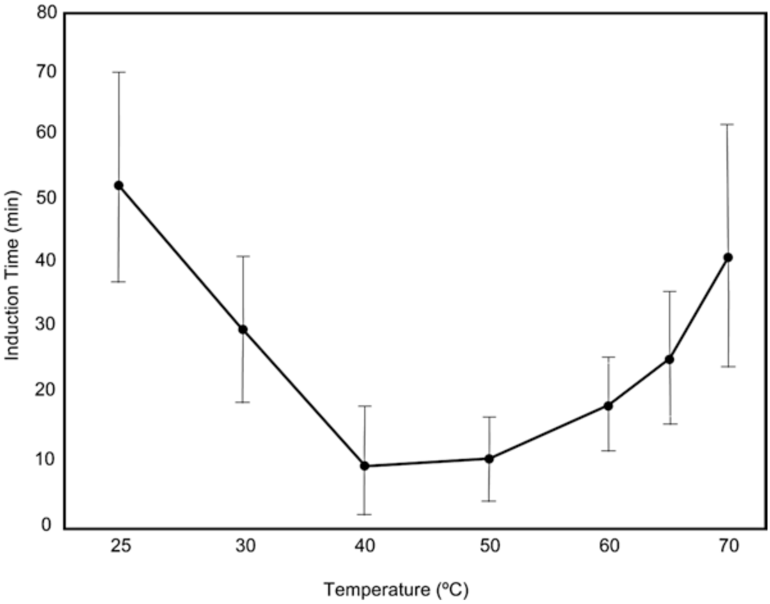

Figure 9.10 Time required for onset of sucrose nucleation for sugar syrup (80: 20 sucrose to 42 DE glucose syrup on solids basis; 20% water content). Syrups were cooled quickly from 80 °C to observation temperature with agitation initiated once syrup had reached desired temperature (With permission from Hartel et al. 2011)

enrobing. Over time, within the package, the invertase acts to reduce the viscosity of the fondant, leaving a softer center within the chocolate coating. Commercially, softening may be slight, as found in many chocolate-covered cream candies, or extensive, as seen in cordial cherry candies.

9.4.2.1 Enzymatic Hydrolysis

Commercial invertase is extracted from yeast by precipitation with alcohol. The extracted enzyme is mixed in glycol to give a commercial solution with standard activity (ability of the preparation to hydrolyze sucrose under controlled conditions).

Invertase (I) is an enzyme that hydrolyzes one molecule of sucrose (S) into one molecule each of fructose (F) and glucose (G), using up a water molecule (W) from the solution in the process, as shown in the following chemical reaction.

$$S + W \xrightarrow{I} G + F$$

As the invertase hydrolyzes the sucrose in the solution phase of a fondant, the concentrations of fructose and glucose in the solution phase increase. Figure 9.11 shows the increase in fructose and glucose content during invertase activity on fondant. Note that the glucose level does not start at zero due to the presence of glucose in the glucose syrup (42 DE glucose syrup was used in this example). The speed of the process is dependent on both formulation and operating parameters, including pH, temperature, invertase concentration, and water content.

The acidity of the fondant solution phase can impact invertase activity. Commercial invertase used in the candy industry has an optimum activity at slightly acidic pH, between 4.5 and 5. The rate of inversion decreases as pH increases to 7 and is sufficiently slow at pH values above 7 to be considered negligible. pH below 3.0 can inactivate the invertase, so proper control of pH is necessary. Ethanol can also inactivate invertase. For this reason the use of alcohol and alcohol based flavorings with invertase in creams must be used cautiously. As a matter of ‘best practices,’ it is always wise to add invertase as the last ingredient in confection formulations.

Temperature is another parameter that influences invertase activity. Since invertase is a protein, temperatures above about 80 °C (176 °F) cause rapid denaturation of the enzyme and subsequent loss of activity. For this reason, invertase cannot be added into the batch formulation prior to cooking the sugar syrup; if cooked in the batch, the invertase will completely denature and lose

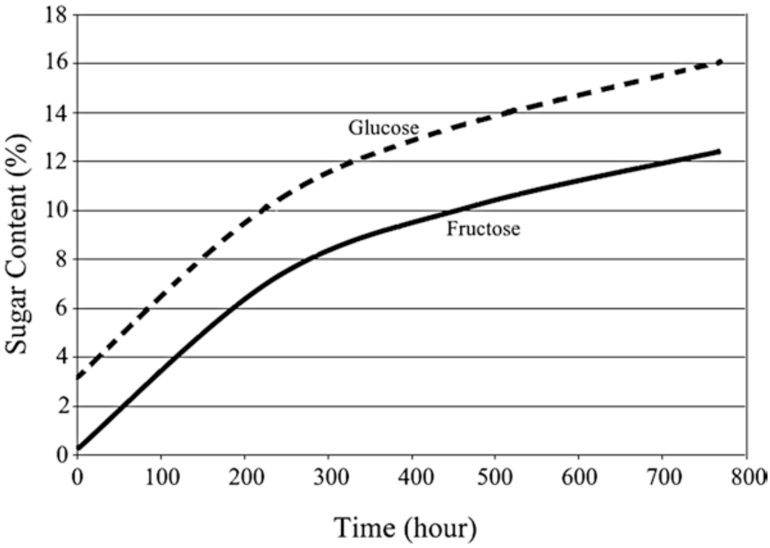

Figure 9.11 Increase in glucose and fructose content during invertase activity in fondant with 16.8% initial water content (80:20 sucrose: 42 DE glucose syrup on solids basis) (From Wu 2006)

all of its activity. The maximum activity, or rate of inversion, occurs at approximately 63 °C (145 °F); however, even at this warm temperature, there is a substantial loss of activity, on the order of 10% over a period of 30 min. Because of this inactivation at warm temperature, the time a commercial cream spends in the remelting stage can have a significant effect on subsequent activity of the enzyme and can lead to less softening of the product than desired (or expected). Adding invertase as late in the process as possible ensures that the enzyme retains maximum activity.

One of the most important parameters influencing invertase activity is the water content of the liquid phase or the inverse of total solids. More correctly, the water activity governs the ability of the enzyme to operate. Sufficient water must be available for the enzyme to be active. If dissolved solids content increases too much during hydrolysis and water activity decreases too much, invertase activity stops. Numerous studies suggest that invertase activity ceases when water activity decreases to about 0.65 (Silver and Karel 1981; Wu 2006), although the exact value may depend on other parameters (i.e., invertase concentration, glucose content, etc.). Some say the limiting condition is when soluble solids in the liquid phase reaches 83%, but the composition of the liquid phase is important in that it determines water activity. Silver and Karel (1981) showed that invertase activity stopped once water activity had fallen sufficiently, but that the enzyme retained activity once water was added back into the system. That is, the enzyme stops because conditions become unfavorable, not because the enzyme is destroyed. It becomes active again if more water is added.

Since one molecule of water is needed to hydrolyze one molecule of sucrose, which is replaced by one molecule each of fructose and glucose, both water content and water activity decline substantially during invertase activity (Figure 9.12). There is a natural inhibition that governs the maximum extent of the invertase reaction, which means there is a maximum level of softening that can occur for each formulation. The end-point of the reaction is dependent on soluble solids content, water activity, and glucose content (product inhibition).

9.4.2.2 Physical Changes Due to Invertase Action

When the invertase hydrolyzes a molecule of sucrose into glucose and fructose, numerous things change in the fondant. The most obvious is the change in concentration of all three sugar molecules, a decrease in sucrose and water concentrations and an increase in fructose and glucose concentrations. In fact, the rate of the inversion reaction can be followed in a fondant

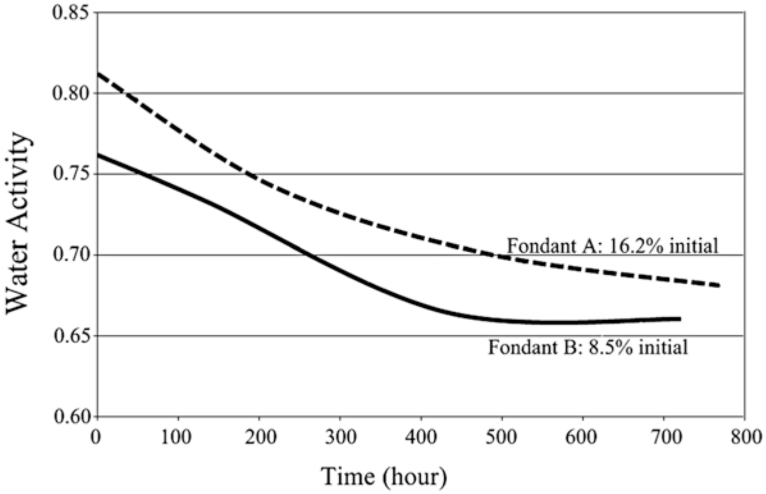

Figure 9.12 Change in water activity during softening of fondant (80:20 sucrose: 42 DE glucose syrup) at room temperature with different initial moisture content by invertase (From Wu 2006)

by tracking the increase in both glucose and fructose (Figure 9.11). However, several physical properties change as these concentrations change, the sum of which ultimately causes the observed softening.

The removal of a sucrose molecule from the solution and addition of glucose and fructose molecules causes a slight shift in phase equilibrium of sucrose. There now is one less molecule of sucrose in solution, which causes the solution to become slightly undersaturated. This means that a molecule of sucrose can now dissolve from the crystalline phase and become part of the solution. Actually, this is not quite a one to one relationship between sucrose molecules hydrolyzed and sucrose molecules dissolved from the crystal, since the addition of the glucose and fructose to solution causes a slight decrease in the solubility of sucrose (see Section 2.8). Regardless of the exact balance, as more and more sucrose molecules in the solution are hydrolyzed by the invertase, more and more sugar crystals dissolve. At the same time, one molecule of water is removed from solution for each molecule of sucrose that is hydrolyzed.

With the change in crystal content and presence of invert sugar, there is a substantial decrease in viscosity and increase in fluidity of the fondant due to the changes in composition. With a decreased content of crystalline sucrose and increased glucose and fructose concentrations in solution, the entire fondant becomes more fluid in nature, despite the slight decrease in water content. For a given molar concentration, glucose and fructose, both monosaccharides, are less viscous than sucrose, a disaccharide. The rate of these changes in physical properties and their extent depend on the properties of the fondant and environment, as noted in the previous section.

9.4.3 Stability and Shelf Life of Fondants and Creams

Fondants can change during storage by losing moisture or, in some rare cases, due to mold growth. Also, over time, the many small crystals can recrystallize, meaning the crystals grow increasingly larger over time, resulting in a coarser fondant. The water activity of fondant is governed by the characteristics of the syrup phase, with water content and total dissolved solids being the important parameters (see Section 3.3).

9.4.3.1 Moisture Loss

The water activity of a commercial fondant or cream product is likely to be between 0.6 and 0.65, but might be as high as 0.75 for very soft fondants. Since environmental relative humidity is often 50% or lower (except in humid climates), there is usually a net migration of moisture from the candy to the air. Thus, fondants and creams generally tend to dry out and harden over time if exposed to ambient air. Even a coating of chocolate does not completely prevent moisture loss, so that chocolate-coated cream centers also harden over time (albeit at a reduced rate). Packaging the candy in materials with water barrier properties and good seals can reduce the rate of moisture loss and extend shelf life.

9.4.3.2 Microbial Growth

Osmophilic molds have been known to grow in conditions where water activity is as low as about 0.65. In sugar solutions, reducing water activity to less than 0.65 generally means the dissolved solids in the liquid phase need to be greater than about 75%. Since sucrose at room temperature has a solubility of about 67%, it is clear that a fondant or cream made with only sucrose cannot be stable to mold growth (soluble dissolved solids significantly less than 75%). This means that other sugars, like glucose syrup and invert sugar, are needed to make a stable fondant or cream.

Stability to mold growth and water loss in fondants and creams are governed by water activity, which depends on the type and amount of dissolved sugars in the amount of water remaining in the final product. Fondant with lower final water content is generally more stable since the water activity is usually low enough that it does not support microbial growth. The lower water activity also limits moisture loss to the air during storage by reducing the driving force for moisture loss (the difference in water activity of the fondant to the relative humidity of the air). To enhance stability of fondant to microbial growth, the proper formulation is necessary to ensure that the liquid phase of fondant has sufficient dissolved solids that its water activity is decreased below about 0.65. In general, addition of glucose syrup with low molecular weight sugars, invert sugar or other humectants helps to retard mold growth and prevent moisture loss during storage. The use of invertase to produce glucose and fructose not only softens the cream, but also helps reduce water activity and extend shelf life against microbial issues.

9.4.3.3 Crystal Coarsening

It has been shown that sugar crystals in fondant grow slowly coarser over time (Lees 1965). According to one study, the percentage of crystals below 16 μm was 98% 1 day after fondant manufacture. This value decreased to 95% after 1 week and to 45% after 1 month of storage. Clearly, the sugar crystals in fondant are quite prone to growing larger over time. However, there may be multiple causes for this coarsening effect. One possibility is that moisture redistribution occurs within the liquid phase of the fondant and this leads to an increase in sucrose crystal size, particularly when moisture loss occurs. However, another mechanism, Ostwald ripening, may also be at work based on the crystalline nature of fondant and no variations in moisture content are necessary for this process to occur.

When crystals of different sizes and shapes are packed closely together, as is the case in fondant and cream, a thermodynamic ripening process can take place. This ripening, or recrystallization, is based on the slight differences in solubility for crystals of different sizes, a phenomenon sometimes called the Gibbs-Thomson effect. It has been well documented that very small crystals, typically less than a few microns in size, are slightly more soluble than large crystals due to a surface curvature effect. Based on this difference in solubility, when two crystals of different sizes are in close proximity, as happens in fondant and cream, the smaller crystal may actually be undersaturated and dissolve, while the larger one is supersaturated and grows. The large crystal appears to grow at the expense of the smaller crystal. This is called Ostwald ripening (Hartel 2001). With millions of crystals packed close together in fondant (some estimates put the average thickness of the liquid phase between crystals as only 0.7–1.0 μm), this scenario repeats itself continuously during storage. The end result is that the mean size of the distribution of crystals increases over time and the fondant becomes coarser to the mouthfeel.

When temperature fluctuates during storage, as when temperature increases during the day and decreases at night, this coarsening is exacerbated (Hartel 2001). In general, when temperature fluctuates, there are subtle changes in fondant as the system seeks to maintain phase equilibrium. That is, when temperature rises, crystals have to dissolve to maintain a saturated solution since solubility increases with an increase in temperature. When temperature goes back down again, the solution is now supersaturated, since it has lower solubility at the lower temperature, and crystals grow. If any small crystals completely dissolve away when temperature is high, they do not renucleate when temperature is lowered and the crystal mass deposits on the remaining crystals. The result is that all crystals get a little larger and the mean size increases with time. This same process is responsible for the coarsening of ice crystals in ice cream, particularly when stored in a frost-free freezer.

Both Ostwald ripening and recrystallization due to temperature fluctuations lead to an increase in mean size over time during storage, a negative consequence in fondants and creams. If crystal coarsening is taken far enough, the fondant or cream may be considered unacceptably coarse. The keys to preventing these effects are (1) to make very small crystals in the first place and (2) then to store the fondant or cream at cool and constant temperature.

9.5 Potential Problems and Trouble Shooting

As with most confections, there are numerous potential problems that can cause decreased quality in fondants and creams. Controlling all of the myriad factors that go into making a good quality fondant or cream is not always easy. In general, problems related to fondants and creams are due either to problems with improper initial formulation, unsuitable processing conditions or problems that occur during storage.

9.5.1 Hard Fondant or Cream

One of the potential problems associated with fondants and creams is that they set into a matrix that is too hard for the desired application. This problem may be caused by formulation or processing factors; ascertaining which mechanism (or combination of mechanisms) is the cause of hardening in a specific situation may not be easy. Among the potential causes for hard fondant, one can include (1) water content that is too low for the desired application, (2) sucrose to glucose syrup ratio that is too high, (3) the sugar crystals have become too large and fused together, or (4) insufficient invertase activity during storage in creams.

There are a number of possible causes for low water content, which means the crystal content is higher than desired and the fondant takes on a hard texture. First, cooking temperature might be too high such that too much water is driven off in processing. Upon cooling, excess sugar crystallizes, leading to hard fondant. Alternatively, the creams may have remained in molding starch for too long so that excess water was driven off in the starch. The result would be cream pieces with undesirably low moisture content, high crystal content, and hard texture.

A high sucrose to glucose syrup ratio can lead to hardened fondants and creams through an increase in the crystalline solids content. Glucose syrup reduces the amount of crystalline sucrose at any water content and softens fondant. Addition of humectants also softens fondants and creams.

Even if water content is satisfactory, the sugar crystals must all be small and uniform to give the desired texture. If the sugar crystals become too large or fuse together, the result can be hardened fondant. The main cause of large fused crystals comes from excessive dissolution of fondant in thinning syrup during manufacture of cast creams. Holding the remelted fondant for too long or at high temperatures causes dissolution of sugar crystals (this is often called fondant melting, but is more accurately termed dissolution). When the cream is cooled, it solidifies into a hard matrix as crystals regrow on existing crystals, often causing bridging between adjacent crystals. Alternatively, the bob syrup use to thin the fondant may contain sucrose concentration that is too high. Upon cooling, the excess sucrose in the thinning syrup crystallizes, fusing particles together and causing hard creams.

Invertase is often used to soften hard fondants and creams during storage. If invertase was not added uniformly, if the product is held at temperatures too cool to allow invertase activity, or if the invertase was inactivated from excessive processing temperatures or incorrect pH, softening over time will not occur. If the activity of an invertase solution is suspected, simple comparison tests of hydrolysis of a pure sucrose solution can quickly determine if this is the cause of the problems or not.

9.5.2 Soft Fondant/Cream

A fondant that is too soft does not hold its shape and is prone to flow or leak through a chocolate shell. Soft fondant is typically due to insufficient crystal content, which can be caused by either high moisture content or inappropriate formulation. High moisture content can be due either to a boiling temperature that is too low or insufficient time in molding starch. If the sucrose content in the initial formulation is too low, there will not be enough crystalline sugar to provide the firmness. Decreasing the amount of glucose syrup or other humectants in the formulation will increase the crystalline content and give a firmer fondant.

Molded creams may be too soft for a number of reasons. For one, the thinning syrup may contain either too much moisture or too little sucrose. Also, excess invertase activity can cause undesirable softening of fondants and creams.

9.5.3 Sticky Fondant/Cream

Fondant that is too sticky is most likely due to high water content or formulating with too many low molecular weight sugars or inversion during cooking. Stickiness in candy often comes from the presence of simple sugars like fructose and glucose, which are extremely hygroscopic. As they pick up moisture from the air, the candy surface becomes sticky and gradually the entire piece softens excessively as the moisture moves into the candy.

If low molecular weight sugars are present in the initial formulation (i.e., high DE glucose syrup or high fructose corn syrup), the final product will be sticky. Inversion of sucrose during processing can also cause this problem. Excessively long cook times or low pH during cooking can lead to undesirable inversion and problem of sticky fondant and cream. Ensuring a neutral pH of the batch can limit problems with inversion during cooking.

9.5.4 Coarse Fondant/Cream

The presence of large crystals in fondant or cream leads to the sensory perception of coarse fondant. Controlling crystallization in fondant and cream is critical to obtaining a smooth product. Large crystals can be caused by a number of factors, including (1) improper beating temperature, (2) insufficient beating energy input, (3) crystal formation prior to beating, (4) insufficient crystal modifier in the formulation, or (5) excessive crystal dissolution in bob syrup method of cast cream formation.

As discussed previously, intense beating of fondant at the appropriate beating temperature is necessary to produce the largest number of nuclei and maintain a smooth fondant. Beating temperatures either too high or too low produce fondant with larger crystals, as does less than adequate beating intensity. Furthermore, if crystals are present in the supersaturated sugar solution prior to beating, these crystals have the opportunity to grow to sizes larger than the critical threshold sensory detection size. To maintain a smooth fondant, all of the crystals should be less than about 15 μm, with the average size less than 10 μm.

Improper formulation can also impact crystal size. According to the data in Table 9.5 (Lees 1965), higher levels of glucose syrup led to smaller crystal sizes, especially when optimal beating temperature of 40 °C was used. In this case, the lower total crystalline content found with the higher level of glucose syrup most likely led to smaller crystals. However, other changes, some of which might be considered negative, also result from using higher levels of glucose syrup.

In the casting method of making creams, the characteristics of the thinning syrup and conditions used for thinning fondant are critical to maintaining the small crystal size in the initial fondant. Any time fondant is heated or thinned with bob syrup, some of the initial crystals are dissolved away. Thus, when heated and thinned fondant is cooled again, there are fewer crystals remaining, which must take up all the crystalline phase volume. This means that all crystals grow a little larger. If too many crystals have been dissolved due to excessively warm temperatures or addition of too much thinning syrup, some of the remaining crystals can grow large enough to be detected in the mouth.

9.5.5 White Surface Discoloration

In certain types of deposited cream candies, a surface discoloration can sometimes form if crystallization is not properly controlled. This problem is most apparent on dark-colored pieces that are not chocolate coated. The problem may arise from uneven heating of the cream prior to depositing. In deposited creams, there is a fine balance between heating sufficiently to reduce viscosity for easy depositing and having sufficiently low temperature to minimize dissolution of the crystals from the fondant. If heating is uneven, a portion of the mass has less crystalline seeds remaining and upon cooling, this region will recrystallize with larger crystals. This results in redistribution of the colors in the region of the larger crystals, leaving white spots or streaks.

Depositing the cream syrup at temperatures above about 82 °C (180 °F) can also lead to discoloration problems, particularly at the flat surface of candy exposed to air (as opposed to the candy in contact with the mold). As the mass cools and sugar crystals grow, there is a release of latent heat from crystallization that focuses on that surface because of the insulating effect of the mold. If depositing temperature is too warm, all seeds in this area may be dissolved by this heat. Without seeds to guide crystallization, the sugar eventually crystallizes randomly as the candy cools, leaving large white spots as the colors are excluded. Careful control of depositing temperature is needed to prevent this problem.

Acknowledgments Thanks to Roger Hohberger (SPEC Engineering), Maurice Jeffery and George Tzakis for technical comments and suggestions.

Appendix A.9.1 Calculation of Crystalline and Liquid Phases of Fondant

The crystal content in fondant can be calculated by use of a mass balance, as shown schematically in Figure 9.13, where the concentrated sugar syrup, F, is converted into a fondant with crystal content, C, and liquid phase, P. To find the amount of crystals, the amount of liquid portion, P, of the fondant, and the composition of the liquid phase, the following steps are used:

- First calculate water, sucrose and corn syrup solids in the feed;
- This also gives water and corn syrup solids in the liquid portion of the crystallized fondant (Equations 2 and 3 in Figure 9.13);
- Find sucrose dissolved in liquid portion, P, from solubility Equation 5;
- Sum water, corn syrup solids and sucrose in liquid portion to get total P;
- Subtract P from 100 to get amount of crystals;
- Calculate total dissolved solids from components of P.

For example, given a fondant with 12% water content (88% dry solids) and a 70/30 dry basis ratio of sucrose to corn syrup solids, the calculations for 100 g of fondant are:

$$W_F = W_p = (0.12)(100) = 12\text{g } H_2O$$

Sucrose is 70% dry solids, which is 88% of total:

$$S_F = (0.7)(88) = 61.6\text{g } \textit{sucrose}$$

CS is 30% of dry solids, which is 88% of total (note that the sum of $W_F + S_F + CS_F = 100$, which it should since we started with 100 g fondant:

Mass Balances (components in = components out):
Assume a basis of 100g fondant.

(1) Total Mass: F = P + C = 100
(2) Water: $W_F = W_P$ assumes no water in crystals
(3) Corn Syrup: $CS_F = CS_P$ assumes no corn syrup solids in crystals
(4) Sucrose: $S_F = S_P + C$ assumes crystals are pure sucrose
(5) S_P [g/100g H_2O] = 210.38 - 0.3424 CS_P [g/100g H_2O] sucrose solubility

Figure 9.13 Mass balance to calculate crystal content and liquid phase concentration in fondant

$$CS_F = CS_P = (0.3)(88) = 26.4\text{g CS}$$

The next step is to determine the amount of sucrose in the liquid portion (P). For that, the concentration of corn syrup solids on a 100 g H_2O basis (for Equation 5) must be known. In P, there is 26.4 g CS and 12 g H_2O, so:

$$\begin{aligned} CS_P &= 26.4\text{g CS} \div 12\text{g H}_2\text{O} \\ &= 2.2[\text{gCS}/\text{gH}_2\text{O}] = 220[\text{gCS}/100\text{g H}_2\text{O}] \end{aligned}$$

Then, from Equation 5:

$$\begin{aligned} S_P &= 210.38 - (.3424)CS_P \\ &= 210.38 - (0.3424)(220) \\ &= 135.05[\text{g } \textit{sucrose}/100\text{g H}_2\text{O}] \\ S_P &= 1.35[\text{g } \textit{sucrose}/\text{g H}_2\text{O}] \end{aligned}$$

But, there are 12 g H_2O in P, so S_P is:

$$\begin{aligned} S_P &= 1.35[\text{g } \textit{sucrose}/\text{g H}_2\text{O}](12\text{g H}_2\text{O}) \\ &= 16.21\text{g } \textit{sucrose} \end{aligned}$$

Now, all components of P are known and they can be summed to get the total of the solution phase of the fondant:

$$\begin{aligned} S_P + CS_P + W_P &= 16.21 + 26.4 + 12 \\ &= 54.61\text{g } \textit{total} \ \textbf{Liquid Phase, P} \end{aligned}$$

From Equation 1, C is found as:

$$\begin{aligned} C &= 100 - 54.61 \\ &= 45.39\text{g } \textit{of crystals} \ \textbf{Solid Phase, C} \end{aligned}$$

Furthermore, the dissolved solids content of the liquid portion, P, can be found as

$$\begin{aligned} (S_P + CS_P)/P &= (16.21 + 26.4)/54.61 \\ &= 0.78 \textit{ or } 78\% \end{aligned}$$

Dissolved solids in P

To summarize, a fondant made with 12% water content and a 70/30 sucrose to corn syrup ratio (dry solids basis), has ***45.39% crystals*** and a ***liquid portion of 54.61%***, as a saturated sugar solution with ***a total dissolved solids concentration of 78%***.

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Caramel, Fudge and Toffee

10

10.1 Introduction

Caramel, fudge and toffee are distinguished from other sugar-based confections by the addition of milk or its components. The presence of milk ingredients during the cooking process generates unique colors, flavors and aromas associated with caramel, fudge and toffee.

Caramels constitute a wide classification of milk-based confections that can vary in texture from a creamy smooth fluid caramel to a hard candy-type caramel, depending primarily on water content. Water content of caramel may be as low as 4–5% and as high as about 18%, with textures that vary accordingly. Caramel with high water content may be fluid and runny, suitable for use as a sauce or for depositing into a mold (i.e., starch mold, starchless mold or chocolate shell). Caramel with very low water content (4%) has a glass transition temperature (see Section 2.9) above room temperature and behaves like hard candy. Many commercial caramels have a water content of about 10%, giving a texture that is firm yet chewy with minimal cold flow.

Caramels also can be either partially grained (5–15% sugar crystals), with a relatively short texture, or ungrained, with a stretchy and chewy texture, depending primarily on the sucrose to glucose syrup ratio. In general, the higher the sucrose content in the formulation, the more likely graining is to occur and the higher the crystal content. In some caramel formulations, lactose may be present at a concentration sufficient to induce lactose crystallization since lactose solubility is only 16% at room temperature (see Section 2.8).

The amount (1–4%) and nature of the protein also influence textural properties since milk proteins aggregate around the emulsified fat globules dispersed throughout the candy mass. This network of aggregated proteins and emulsified fat globules helps provide structure and prevent caramel cold flow. However, under certain circumstances, particularly with low pH ingredients and higher levels of milk solids, excessive protein aggregation can occur, giving a grainy, tapioca-like texture. Control of pH is important to controlling the protein to obtain the desired texture and caramel characteristics.

During caramel cooking, color and flavor formation occur through either the Maillard browning reaction, a reaction between reducing sugars and proteins, or caramelization of sugars. Many commercial caramels are made by first blending all the ingredients followed by cooking the pre-mix directly to the desired temperature. Maillard browning dominates color and flavor formation in these caramels. Low pH also reduces the Maillard browning pathways, so again, control of pH in the caramel pre-mix is important to caramel quality. Other caramels, the so-called burnt sugar caramels, are made by first caramelizing

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the sugars at very high temperatures before adding the dairy ingredients. Here, caramelization of sugars provides more of the colors and flavors.

Technically, fudge is highly grained caramel, with typically about 25–30% sugar crystal content. The numerous sugar crystals impart a softer texture than found in caramel. Moisture content normally is in the range of 10–12%. Graining in fudge may be accomplished by agitating the cooked candy mass to induce crystallization in the same manner as graining of fondant. Alternatively, fondant may be used to seed the concentrated sugar mass to make fudge.

Toffee is a term that has different meaning in different parts of the world. In some countries, toffee is used to denote a chewy caramel-type candy, whereas in other countries, toffee is more like a brittle candy (e.g., peanut brittle) with higher fat content. Toffee (as found in the United States, and often called English toffee) differs from caramel and fudge in that it contains almost exclusively sugar (no glucose syrup) and butter, and is cooked to high temperatures similar to hard candy. Due to the high cook temperatures, toffee generally has low water content, from 3% to 6%, and therefore, has similar texture as hard candy. The emulsified fat in toffee results in a brittle texture that is easily broken down in the mouth. The lack of protein in toffee and the high cook temperature means that flavor and color development occurs primarily from sugar caramelization (rather than Maillard browning), although cooked butter flavors also impart specific characteristics to toffee. In this chapter, toffee will refer to a brittle-like product made primarily with sucrose and butter.

10.2 Formulations and Ingredients

Caramel, fudge and toffee typically contain sweeteners and dairy components, along with other ingredients to either enhance flavor, texture or shelf life. Typical formulations are shown in Table 10.1. The ingredient composition and final water content are chosen to impart the desired textural characteristics.

10.2.1 Sweeteners

As with many confections, sucrose and glucose syrup are the primary sweeteners of caramel and fudge. They provide the bulk of the confection and contribute to the unique texture. Typically, 42 DE glucose syrup is used in caramel and fudge. A lower DE corn syrup gives a harder, chewier texture, whereas a higher DE corn syrup leads to stickiness and cold flow, with the effects being primarily attributed to the effect on viscosity of the continuous phase. Invert sugar, high fructose syrup or high DE glucose syrup may be added (4–5%) to give a more tender texture and to control crystal size in grained caramel and fudge. Invert sugar and high fructose syrup also act as humectants to hold water and extend shelf life. However, if too much invert is present, the product will be sticky and prone to cold flow. In some caramel recipes, brown sugar also may be added to contribute specific flavor effects.

The ratio of sucrose to glucose syrup has a significant effect on the texture and characteristics of the finished caramel or fudge. For one, the ratio of sucrose to glucose syrup governs the extent of sugar crystallization. If an ungrained, chewy product is desired, higher glucose syrup levels are required to prevent sugar crystallization, whereas the sucrose content must be sufficiently high in grained caramel and fudge to allow the desired crystal formation. Higher levels of glucose syrup also promote a tough and chewy texture in the caramel.

Caramel and fudge also generally contain lactose through addition of milk ingredients. Lactose content depends on the type of milk ingredient used and its concentration in the formulation. Less expensive dairy sources, like whey, introduce greater amounts of lactose and this may affect various attributes, such as color development and shelf life. Due to its low solubility, lactose graining is more prone to graining than sucrose in caramels with high lactose content.

Table 10.1 Typical batch formulations (in %) for caramel, fudge and toffee

	Commercial caramel (ungrained)	Caramelized sugar caramel	Fudge	English toffee (American)
Water	15–25	0	10–15	8–10
Sucrose	10–20	55–65	30–50	45–55
Glucose syrup (42 DE)	36–46	0–5	10–20	0
Sweetened condensed milk[a]	20–40	0	12–20	0
Cream	0	25–35	0	0
Butter[b] (fat)	5–15	6–12	8–16	40–50
Fondant	0	0	3–5	0
Chocolate liquor/cocoa powder	0	0	0–10	0
Salt	0.2–0.5	0.2–0.5	0.2–0.5	0.3–0.6
Vanilla	0.1–0.3	0.1–0.3	0.1–0.3	0.1–0.3
Lecithin	0–0.4	0–0.4	0–0.4	0.25–0.45
Nuts (unroasted)	0	0	0–12	6–12

[a] Other dairy ingredients might include evaporated milk or dried milk powder

[b] Salted butter needed for toffee

Sugar-free versions of caramel and fudge can be found, where a sugar alcohol (sorbitol, mannitol, maltitol, isomalt, lactitiol and xylitol) replaces sucrose and some longer-chain polymeric sweetener, such as soluble corn fiber, polydextrose, or hydrogenated starch hydrolysate (HSH), replaces glucose syrup. High-intensity sweeteners may be needed in sugar-free caramels and fudge. Sugar-free caramel or fudge in the United States is required to have less than 0.5 g of mono- and disaccharides per reference serving size. Thus, milk ingredients must be replaced (i.e., by use of caseinates, protein isolates and gums) to eliminate the lactose. However, without lactose or other reducing sugars, browning reactions do not occur and the candy must have appropriate color and flavor added.

English toffee generally contains only sucrose as the sweetener, with no glucose syrup or invert sugar added. Some inversion of the sucrose occurs due to the high cook temperature, providing a measure of control over sucrose graining.

10.2.2 Dairy Ingredients

A key component in caramel and fudge is the milk ingredient since it is the primary contributor to color, flavor and texture (Galloway 2003). Milk contains approximately 12–13% solids (87–88% water), which include 3.5–3.8% milk fat, 4.7–4.9% lactose, 3.0–3.5% protein and 0.5–0.9% ash (minerals and vitamins). Each of the components of milk play an important role in caramel and fudge quality so careful control of the dairy ingredient is necessary to make a consistent, quality product. In fact, some say that caramel processing is a controlled scorching of the milk to give a product with the desired color, flavor and texture.

In many caramels, it is the Maillard browning reaction (see Section 1.4.3.1) that gives the desired color and flavor. The milk ingredient in caramel provides both the protein and one of the reducing sugars (lactose) for the Maillard browning reaction (note that the reducing sugar, glucose, is also present from addition of glucose syrup and that invert sugar may be formed during cooking). The complex set of reactions as protein and reducing sugars are heated together results in formation of various coloring and flavoring molecules.

Milk proteins, namely caseins (80% of proteins in milk) and the whey proteins α-lactalbumin and β-lactoglobulin (20% of proteins in milk), also contribute to the textural characteristics of caramel (see Section 10.4.2). During caramel cooking, the whey proteins are partially denatured, complex with casein micelles and form an aggregate structure around the fat globules. These protein aggregates help to provide viscosity, enhance stand-up properties, and prevent cold flow in caramels. Caramel should be formulated to contain between 1% and 4% protein to ensure sufficient protein aggregation. Fresh milk contains about 3–3.5% protein, with concentrated milk products containing respectively higher levels.

Numerous dairy ingredients can be added to caramel and fudge, with each giving slightly different quality and texture. Sweetened condensed milk, evaporated milk, dried milk powders and even the different forms of whey are often used. Cream and half and half also can be used for caramel production, although for the most efficient processing of caramel, milk must be concentrated in some way to remove water prior to addition to the caramel batch.

One of the main criteria for making consistent caramel and fudge is that the milk ingredient be consistent; specifically, the state of the milk proteins should always be the same. Variable heating of milk during processing (i.e., concentration or drying) may lead to differences in the protein's capability to form a network in the caramel upon cooling. Whey proteins in particular are sensitive to extended and repeated heating. When temperatures go above 65–70 °C (149–158° F), as is often found in high temperature, short time pasteurizers, whey proteins are denatured and complex with caseins. These changes can impact the characteristics of the protein-carbohydrate interactions that determine the textural properties of caramel (Bondi et al. 1993).

Appendix A.10.1 provides composition data for a variety of dairy ingredients that could potentially be used in caramels and fudge.

10.2.2.1 Sweetened Condensed Milk

Sweetened condensed milk is defined by the Standard of Identity in the Code of Federal Regulations (21 CFR 131.120).

> Sweetened condensed milk is the food obtained by partial removal of water only from a mixture of milk and safe and suitable nutritive carbohydrate sweeteners. The finished food contains not less than 8% by weight of milkfat, and not less than 28% by weight of total milk solids. The quantity of nutritive carbohydrate sweetener used is sufficient to prevent spoilage. The food is pasteurized and may be homogenized.

To make sweetened condensed milk, whole milk is evaporated and sugar is added in the form of fine crystals. The combination of evaporation plus sugar addition reduces the water content to about 27% and the water activity is lowered to the point (<0.88) where sweetened condensed milk is relatively stable to microbial growth for long periods of time. However, this water activity is not low enough to completely prevent mold growth so that sweetened condensed milk should be stored in the refrigerator to extend shelf life to a couple months. However, refrigerated temperature storage may lead to crystallization of lactose in sweetened condensed milk. It is always a good idea to make sure that sweetened condensed milk is well-stirred prior to use so that all components are homogeneous prior to use.

Sweetened condensed whole milk (about 7.5% protein) gives a smooth, creamy texture to caramel with a rich mouthfeel. Sweetened condensed skim milk (about 10% protein) can also be used in caramel formulations, allowing some flexibility in fat addition (butter or vegetable fat).

10.2.2.2 Evaporated Milk

Evaporated milk (about 7% protein) without the addition of sugar can be used in caramel manufacture, although the high water content (about 70%) means more water has to be removed during cooking of the candy mass. The high water activity means condensed milk is not stable to microbial growth and must either be canned for later use or used shortly after production. Evaporated milk imparts a rich creamy flavor to caramel, but its addition to the formulation can be problematic due to the high water content. It is often added slowly after the batch has begun to boil in order to prevent curdling of the proteins or excessive color development due to the longer cook times needed to remove the excess water.

10.2.2.3 Dried Milk Powders

Milk, either whole or skim, is dried by first concentrating it in an evaporator followed by drying it into a powder. Spray dried milk powders (about 26 or 36% protein for whole or skim milk powder, respectively) are most common, although roller dried milk powders are available as well. Low heat spray dried milk powders are often used in caramels since high heat causes excessive protein denaturation. Because of the degradation to the protein during drying, caramels made with dried powders typically have lower quality; they are less smooth and have inferior flavor and cold flow compared to caramels made with sweetened condensed milk.

Milk powders also must be rehydrated prior to use in caramel. Typically, the milk powder is added with the granulated sugar and then dissolved in warm water with high shear mixing. It may take up to several hours to ensure complete hydration of the proteins. Rehydrated powdered milk may also be homogenized prior to use to enhance the smoothness of caramel.

10.2.2.4 Cream

Cream, the result of skimming milk, may be added to produce excellent high fat caramel and fudge. Cream, with about 40% fat, 2–3% protein and 50–60% water, gives a caramel with excellent milk flavor and soft texture. The relatively high water content of cream, however, means that additional time is required to boil off water to reach the final moisture content. Besides being inefficient, the extended boiling time may cause undesired (excessive) color and flavor development. Dried cream may be reconstituted with warm water for use in caramel and fudge.

10.2.2.5 Whey Products

Whey products are often added to caramels because they provide a cost savings over more expensive milk ingredients. Whey, the liquid remaining after milk caseins are made into cheese, contains primarily whey proteins (α-lactalbumin and β-lactoglobulin), lactose and numerous salts, but also has numerous other minor components (e.g., sphingolipids, lactoferrin, etc.) with potential functional benefits. It can be highly variable dependent on the cheese make process.

Numerous whey products may be used in caramel. Typically, whey proteins are generally removed from whey by ultrafiltration to produce whey protein concentrates and isolates. Whey permeate, the liquid product that passes through the membrane, contains primarily lactose and salts. Salts may be removed to produce demineralized whey. Whey is often dried to produce a whey powder for use in caramels. Any or all of these whey products may be used, although different flavors and textures may result depending on the specific whey product in the formulation.

Caramels made with high levels of whey tend to be darker than normal due to the enhanced browning capability of lactose (a reducing sugar). Also, whey proteins have significantly less impact than casein on stand-up properties, meaning that caramels made with high whey protein and low casein levels are more prone to cold flow.

10.2.3 Fats

Fats make an important contribution to the flavor and texture of caramel, fudge and toffee. The fat is emulsified into small droplets that are dispersed throughout the candy mass. The small fat globules provide lubricity in the mouth during chewing and contribute to the smooth mouthfeel. They also allow for easier processing by preventing stickiness of the candy mass. Fats also provide unique flavors to a confection by carrying lipid-soluble volatile compounds like ketones and aldehydes.

The fat content in caramel and fudge may vary from 6% to 20%, although somewhere between 8% and 15% is most common. Sufficient fat content is needed to provide lubricity to the candy and to impart desirable flavor release, whereas too high a fat content can lead to oil separation and a greasy texture. This is particularly true in toffee where fat content is 25–40% and there are no proteins to help stabilize the fat globules.

10.2.3.1 Butter/Milk Fat

Milk fat is the traditional fat source used in caramel, fudge and toffee. In caramel and fudge, milk fat is added through the dairy ingredient, such as cream, evaporated milk or sweetened condensed whole milk. In some formulations, butter or anhydrous milk fat may be used separate from the dairy protein source. Butter contains about 80% milk fat, with the remaining 20% aqueous phase including water and the proteins, lactose and minerals normally found in milk (see Table A.10.1). Anhydrous milk fat may be made from cream by breaking the emulsion and separating the aqueous phase or by clarifying butter. In toffee, salted butter is the most common fat source.

Beyond the textural contributions provide by fat, milk fat also provides a unique flavor characteristics to caramel, fudge and toffee. Milk fat, when heated in a sugar matrix, produces cooked butter flavors that enhance the creamy taste and texture of these products. Milk fat has ideal properties for caramel and fudge. It melts at about mouth temperature (≈35 °C/95 °F) and has a moderate solid fat content at room temperature (see Chapter 4). The melt temperature ensures that milk fat in caramel melts in the mouth and does not contribute to a waxy sensation.

One danger of using milk fat in caramel, fudge and toffee is development of rancidity during storage due to lipid oxidation. The presence of oxygen and certain metals (as catalyst) promotes degradation of fats, leading to off-flavor generation. For more on lipid oxidation, see Section 4.2.3 for details on mechanisms of oxidation and Section 10.5 on shelf life issues in caramel.

Due to the relatively high price of milk fat and butter, many manufacturers replace either part or all of the milk fat in caramel and fudge with a vegetable fat, in part to reduce costs and in part to protect against rancid off-flavor development.

10.2.3.2 Hardened Vegetable Fats

Caramel and fudge are often made with vegetable fats, sometimes in combination with milk fat to reduce costs. Vegetable fats help provide lubrication, both in the mouth and in processing equipment, although they generally do not contribute to the flavor as much as milk fat. These oils must be highly refined and deodorized so as not to bring undesirable flavors to the confection. Various fats and oils such as soy, palm, palm kernel and/or coconut may be used in caramels. While partially hydrogenated fats were common in the past, efforts to remove *trans* fats have led to their replacement with *trans*-free modified fat blends of either interesterified or fractionated fats.

The melting profile of modified vegetable fats for use in caramels, fudge and toffee should be similar to that of milk fat, although it may be tailored for specific needs. Typically, melting points are between 33 and 41 °C (92 and 105 °F). Higher melting points increase firmness and decrease flavor release, whereas lower melting points decrease firmness. The firmness of a caramel is dependent, to some extent, on the hardness (melt point) of the fat used since the fat globules act as a filler in the protein-carbohydrate matrix. Furthermore, the solid fat content profile of the fat (see Section 4.3.2.2.1) also plays a somewhat minor role on caramel texture and flavor release.

One advantage of using hardened vegetable fats is that lipid oxidation can be controlled. Rancidity developed from exposure of fat to oxygen (see Section 10.4.3.1) produces off-flavors deleterious to the quality of caramel and must be avoided. The higher saturated fat levels of hydrogenated or fractionated vegetable fats compared to milk fat means that caramels made with vegetable fats are slightly more resistant to off-flavor development.

10.2.4 Emulsifiers

Since caramel, fudge and toffee contain a considerable amount of fat (up to 40% fat in toffee), an emulsifier is often needed to control the lipid phase. The most common emulsifier used in caramel, fudge and toffee is soy lecithin, a phospholipid separated in the degumming step of refining soybean oil (see Section 4.6.2.2). Lecithin is typically added at a level of about 0.25%. Sometimes mono- or diglycerides, such as glycerol monostearate (GMS), are used in caramels, particularly when fat content is low. GMS is also known to decrease the stickiness of caramel.

The emulsifier, which situates at the oil/water interface, reduces the interfacial tension between the oil and water. This allows formation of a dispersion of small fat globules when shearing or agitation is applied. The small fat globules, varying in size from about 1 micron to 40–50 μm depending on homogenization, are uniformly dispersed throughout the candy matrix. The emulsifier also helps to prevent coalescence of the emulsion droplets at high temperatures during processing. This is particularly important in English toffee since there are few proteins available to assist in emulsion stabilization. The increase in the viscosity of the candy mass upon cooling ultimately stabilizes the emulsion droplets in the final candy.

10.2.5 Hydrocolloids

In some cases, hydrocolloids like gelatin, pectin, flour or starch are added to provide specific textural effects in caramel. These components, added at relatively low levels (up to 5%), alter the mouthfeel by changing (or replacing) the protein-carbohydrate structure. Pectin and gelatin may be added to provide a chewier texture, whereas starch provides a shorter texture. An egg albumin foam may be added to lighten the texture and color of the caramel.

When starch is added to caramel, it must be gelatinized to impart the desired textural effects. Intact starch granules, unless there are many of them, have little effect on texture. The starch is added to the liquid phase, along with sufficient water to allow gelatinization during cooking. Upon cooling, the gelatinized starch interacts with, or replaces some of, the protein network of the caramel. However, since gelatinized starch has a cleaner breaking point than proteins, caramels made with gelatinized starch have a less chewy texture.

10.2.6 Salts

Caramel pre-mix should have as close to neutral pH as possible to minimize the potential of protein aggregation. The isoelectric point of casein is about 4.7; at this pH, caseins aggregate due to the neutralization of the charges that keep the micelles apart. The combination of a reduced pH and heat during cooking also causes denaturation of whey proteins and their subsequent complexation/aggregation with caseins. To prevent this, salts such as sodium bicarbonate (baking soda), disodium phosphate or sodium citrate (where permitted) may be added at low (0.3%) levels. Some of these salts may also have Calcium-sequestering properties, influencing the nature of the casein micelle, and thereby influencing protein aggregation.

A decrease in pH can be caused by either natural aging of the dairy ingredient or from addition of an acidic ingredient (pectin, certain glucose syrups, etc.). Although some protein aggregation is desired in caramel to provide stand-up properties, excessive aggregation leads to a grainy texture. This type of grainy structure gives a distinctly different texture than sugar graining. Protein grain is often described as a soft grain, giving a tapioca-like texture to the caramel. Excessive protein aggregation can also potentially cause a decrease in the protein stabilization of emulsion droplets. Reduced pH may also negatively affect the Maillard browning reaction.

10.2.7 Added Flavors

Most caramel and fudge formulations call for vanilla flavor to complement the caramelization products and cooked butter flavor. The added vanilla flavor may be either natural, as in vanilla extract, or artificial, with vanillin being the most common. Vanillin can be added during the cook, but vanilla extract is always added after cooking in order to retain the desired flavor notes. A small amount of salt (0.25–1.0%) is generally added as a flavor enhancer. Salt may be added in the cook step or sprinkled on the caramel surface after forming.

Other flavors that may be added to caramel include molasses, honey, chocolate liquor or cocoa, licorice, and raspberry. Numerous flavors of fudge can be found, including chocolate, maple, peanut butter and so on. These flavors are generally added after the cook to prevent loss or change of flavor. When chocolate liquor or cocoa is added after the cook, usually the batch needs to be cooked to a slightly (1 °C; 2 °F) lower temperature to maintain the same texture as those without these added ingredients. Note that adding cocoa or chocolate liquor prior to cooking leads to a caramel with a brownie-like flavor.

Some of these flavors also influence the color of caramel or fudge. For example, the use of chocolate liquor or cocoa to provide chocolate flavor also enhances a deep brown color. The use of natural flavors (fruit purees, etc.) may also influence color.

In caramels and fudge made with vegetable fat instead of butter, cooked dairy flavor may be added in the form of concentrated or enzyme modified dairy flavors. This adds some creaminess back to the caramel.

10.2.8 Added Colors

Since the color of sugar-based caramel and toffee is generated from browning reactions, for the most part, no additional colors are needed. Sugar-free caramels and fudge typically require addition of caramel coloring to provide the desired brown appearance.

In flavored fudges, colors may be added to match the flavor. For example, orange color (FD&C dyes) may be added to a pumpkin-flavored fudge, or pumpkin puree can be added to provide color (and flavor). Typically, FD&C colors, in either water or oil-soluble form, are the simplest to add because they are effective and stable. Powdered colors may not be homogeneously mixed and may result in specking. The use of exempt (natural) colors generally requires higher concentration levels and pH/temperature stability must be considered.

10.2.9 Inclusions

Many caramels and fudges contain particulate inclusions to enhance flavor, texture and/or appearance. These inclusions might include chopped nuts, raisins, coconut, chocolate pieces, marshmallows, and crisp rice. In toffee, chopped nuts, like almonds, are usually included. Potential negative effects of such inclusions are changes in texture due to moisture equilibration, initiation of sugar crystallization (graining), or lipid oxidation from lipase activity (particularly from nuts).

10.3 Processing

Figure 10.1 shows the general steps necessary to make caramel and fudge. In general commercial operation, the process for making classic caramel and fudge involves mixing all of the ingredients, homogenizing the fat and cooking to the appropriate temperature to obtain the desired water content, followed by cooling and forming. Sufficient time at elevated temperature (above about 110 °C (230 °F)) is needed to allow time for the browning reactions. Numerous strategies for inducing browning are used, with each variation leading to slightly different flavor generation depending on the relative contribution of Maillard browning or sugar caramelization.

Another approach for making caramel is the caramelized or "burnt sugar" approach. While there are several approaches to making this caramel, they all involve heating sugar to very high temperatures (177–182 °C (350–360 °F)) to cause melting. Continued heating promotes caramelization and a dark rich flavorful color is

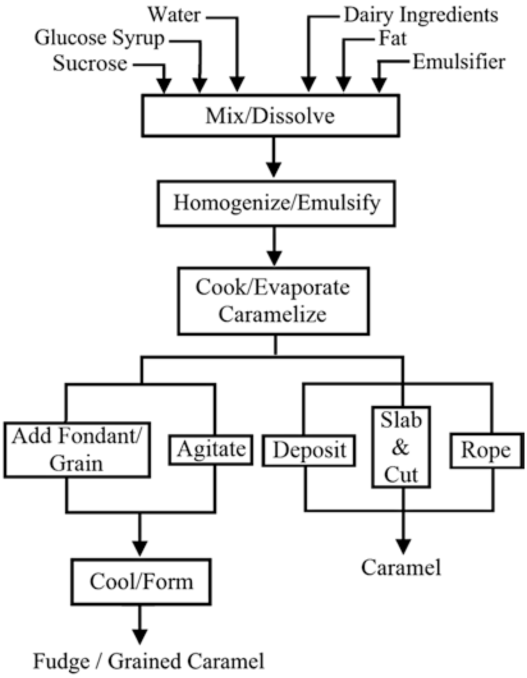

Figure 10.1 Schematic for manufacture of caramel and fudge

observed. Often, an acid such as lemon juice is added at the beginning of the cooking process to help promote sugar inversion and caramelization. As the sugar starts to melt, stirring is stopped to prevent crystallization. After the sugar has browned, the dairy ingredient, often warm cream, is added to cool the mass and add its own flavor notes. The flavors produced in this approach may be somewhat different from that of the typical commercial cooking operations due to the primary contribution of caramelization over Maillard browning. This approach is most often used on small batches of high quality caramel. Other advantages include the fact that no stirring is needed and no protein burn-on occurs since the dairy portion has not yet been added.

The process for making toffee is shown schematically in Figure 10.2. This process is similar to that for making hard candy in that the ingredients are mixed, cooked to high temperature to leave low residual water content, and then cooled to allow formation of a glassy sugar matrix. Unlike hard candy, however, toffee has no glucose syrup added and so the sugar may go through a graining and re-melting process prior to reaching the final cook temperature. Inversion of sucrose during cooking provides a small measure of control over sugar graining.

Manufacturing of caramel, fudge and toffee may be either batch or continuous. Batch processing is often accomplished in a single vessel for mixing and heating, whereas continuous processing requires moving the candy mass from one operation to the next in the most efficient manner. Although there are some slight differences in processing steps for caramel, fudge and toffee, they all follow essentially the same steps – mixing, cooking and development of color/flavor, cooling, ingredient (flavors, powdered seeds, fondant, etc.) addition, forming and packaging. Control of the manufacturing steps for caramel, fudge and toffee is important to obtain consistently high quality candies. Any variations in either the ingredient additions or the processing conditions may lead to changes in the final product.

Rework, defined as product deemed safe to eat but of unacceptable quality, can be added back into the formulation for caramel or fudge. As long as the color, texture and flavor of the rework material is suitable, it can be added at levels of up to 5% or so of the product mass. The rework product can either be melted directly in the cooked batch or redissolved in water and added to the pre-mix vessel (typically the preferred mode). It is important to ensure that no crystals remain in the mix due to addition of rework in order not to cause undesired graining.

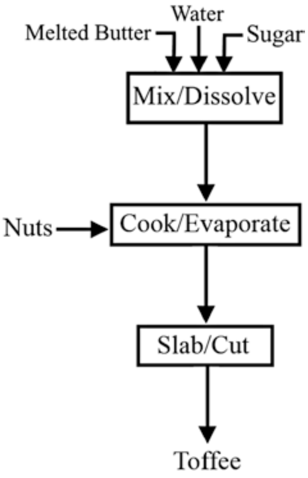

Figure 10.2 Schematic of process for making toffee

10.3.1 Mixing and Emulsification

In small batch systems, sucrose, glucose syrup, milk ingredients and water are often added to the tank and heated to about 71–82 °C (160–180 °F) allow complete dissolution of the granulated sugar and melting of the fat. Complete dissolution of sucrose crystals is particularly important in caramels and fudge to prevent undesirable graining so sufficient time at warm temperatures are needed. Sufficient water, usually 18–22% of the batch, is also required in the pre-mix to ensure sugar dissolution. Depending on the milk source, it may be added completely at the start of the batch or added slowly during the course of cooking. The candy pre-mix may be vigorously sheared, either by hand or with a submersible mixer, to emulsify the fat in the aqueous sugar solution. Hand mixing results in fairly large fat globules, perhaps as large as 100 μm, with a fairly wide spread of droplet sizes. Submersible mixers can bring the droplet size down to about 20–30 μm, again with a fairly wide range of droplet sizes. In larger batch systems, steam jacketed, scraped surface kettles are often used for mixing and emulsification.

In continuous systems, large pre-mix tanks heated by steam are used to mix and dissolve sugars, milk ingredients and fat. Extra water may be needed depending on the form of the ingredients and their relative contribution to the formulation. Again, sufficient time at intermediate temperatures is needed to ensure complete dissolution of the sugars. Once the sugars are dissolved and the fat is melted, emulsification may take place in the pre-mix tank through use of high-intensity mixers or in continuous emulsifiers, which are typically mechanical mixers that shear the pre-mix as it is pumped through the unit. Alternatively, homogenizers may be used to emulsify the fat. In a homogenizer similar that that used for breaking down fat globules in milk, the fluid pre-mix is forced (pumped) through a narrow orifice under high pressure to break down the liquid fat droplets into small globules (1–10 μm in diameter) with a narrow size range. The output of the continuous emulsifier or homogenizer feeds directly into the continuous cooker.

10.3.2 Cooking and Browning

In both small and large batch cooking systems, heating continues after emulsification until the boiling temperature reaches the necessary value to give the desired water content. Because of the added lactose and salts from the milk ingredients, the correlation between boiling temperature and final water content is not as well-defined as for sugar syrups (see Section 2.2) although the process generally follows the same principles. In general, cooking temperatures of 110–115.5 °C (230–240 °F) at sea level give softer and more fluid caramels with higher water content (10–15%). Cooking to 118–120 °C (245–248 °C) gives medium firm caramel with water content of 9–10%. Cook temperatures of 121–124 °C (250–255 °F) give caramels with a firm texture at water content of 7–8%. Cook temperatures of 128–131 °C (262–267 °F) give hard caramels with low (6%) water content. Caramel hard candies are cooked to 146–149 °C (295–300 °F) to reach the glassy state. Some recent research findings (unpublished) have shown that high protein content in the formulation can influence these correlations between cook temperature and water content, most likely through their effect on evaporation rate prior to boiling. Formulations that contain greater than 5% protein should be critically evaluated for the proper cook temperature to attain the desired moisture content and texture.

Fudge typically is cooked to 114.4–115.5 °C (238–240 °F) to give a water content of 10–12%, whereas toffee is cooked to 149–154 °C (300–310 °F) to reduce water content to less than 3%. Some toffees are cooked to temperatures as high as 157–160 °C (315–320 °F) to give a dark color and a brittle texture (lower water content). Slight changes in cook temperature can lead to significant changes in product texture due to the differences in water content; thus, it is critical that cook temperature is carefully controlled to ensure the desired product texture. Since barometric pressure can have a small effect on the final moisture content (see Section 2.7), some candy makers adjust their cook temperature according to outside pressure.

Small-scale batch operations typically utilize small cooking kettles, with sizes from a few kilograms to perhaps 45 kg (≈100 pounds) of product. High temperature at the kettle surface can lead to scorching, or formation of black specks of caramelized sugars and denatured proteins, if the heat transfer surface is not regularly and efficiently scraped. This is particularly a problem for copper kettles heated over a gas flame, with hand mixing. Good mixing technique is required to minimize scorching. Stainless steel kettles with steam jacket control are often used to minimize milk scorching. Larger operations might typically cook in mixing kettles that can hold hundreds of kilograms of candy with sufficient agitation (scraped or swept-surface mixers) to provide good heat transfer without scorching (Figure 10.3). In scraped-surface, gas-fired mix-

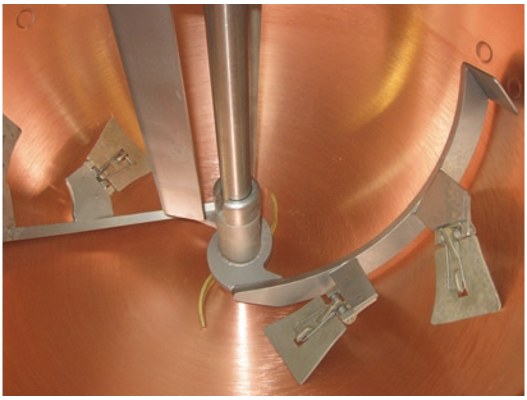

Figure 10.3 Scraped-surface blades in a batch cooking kettle (Courtesy of Savage Bros.)

ers, the level of the boiling mass should be above the scraper blades to prevent scorching/burning and potential graining. In steam kettles, the boiling mass should be above the steam jacket level for the same reasons. Scraped surface mixers continuously remove the viscous fluid on the heat transfer surface to prevent scorching, which can introduce dark black specks into the otherwise creamy brown color.

In batch cooking of caramel and fudge at atmospheric conditions, the time to reach the desired cook temperature is moderated so that sufficient time is allowed to give the desired browning reaction. Typically, at least 20 min of heating (and up to 1 h) is needed to develop the desired color and flavor through the Maillard reaction. Longer heating times give darker colors and stronger caramel flavors, but also cause greater inversion of the sucrose and can potentially lead to stickier product.

In batch processing of toffee, agitation of the mass during cooking must be done carefully so that the fat emulsion is not broken. Coalescence of the fat globules during cooking leads to separation of the fat as an oil phase on the surface. Once oil separation has occurred, it is difficult to regain the emulsion state. Sometimes, addition of a small amount of lecithin along with continued mixing can re-emulsify the fat, at least to some extent.

Larger caramel manufacturers utilize continuous operations. There are numerous designs of continuous caramel cookers. These designs may be as simple as large, heated kettles with multiple sections and weirs to provide a continuous flow pattern and control over residence time. Or, they may be much more complex to independently control the cooking (evaporation of water) process separate from the browning step.

The first continuous caramel cookers were essentially designed to mimic batch cookers, with the candy mass traversing through the cooker as water was boiled off. Color and flavor developed as the candy made its way from beginning to end of the unit, with the residence time within the cooker regulated to produce the desired caramel color and flavor. Modern continuous cookers typically now separate the cooking process from development of the caramel color and flavor to efficiently control both operations. Caramel color and flavor development can either come before (pre-caramelization) or after (post-caramelization) the cooking step.

One of the most common methods of continuous caramel production is the scraped (or swept) surface heat exchanger (SSHE), which can be arranged for either horizontal or vertical flow. A typical SSHE is constructed of two concentric cylinders with the sugar mass flowing through the central core and steam condensing in the annular space to provide the heating. Rotating scraper blades (sometimes called a mutator or a dasher) continuously remove the heated fluid at the heat transfer surface to mix with the fluid in the center. The agitation and scraping (or sweeping) of the surface prevent scorching of the caramel pre-mix. The steam condensing on the outside of the heat exchanger barrel causes heating of the candy mass as it moves through the heat exchanger. In some designs, there may be a scraped internal heating tube in addition to the outside barrel, as seen in Figure 10.4. Micro-film cookers can also be used to quickly and efficiently remove water from the candy syrup.

The residence time of the candy mass in a continuous cooker is very short, often less than a minute, so there is insufficient time for browning. The color of the product exiting a typical continuous cooker is light brown at best, not the desired dark brown caramel color, and the flavors associ-

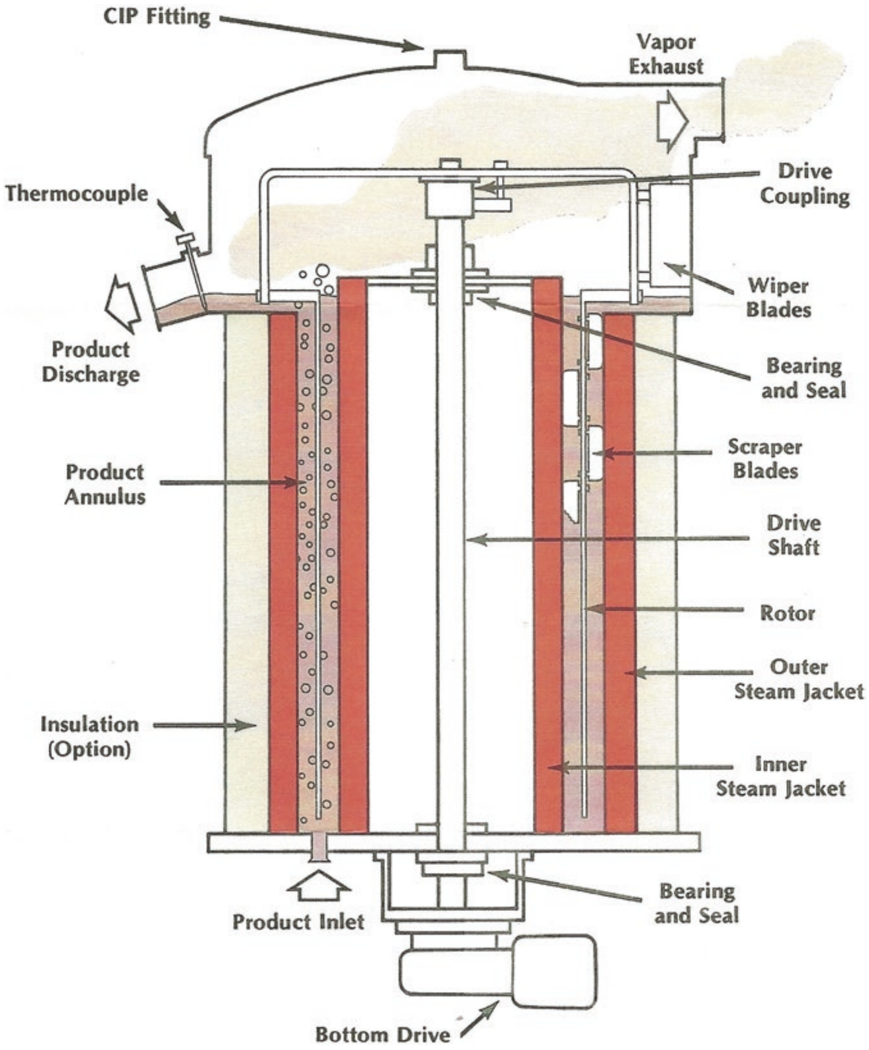

Figure 10.4 Continuous cooker/evaporator (Courtesy of Unified Brands)

ated with caramel candies are not developed. Thus, the output from the SSHE is typically fed into a "caramelizer" unit where the desired color and flavor are developed. This arrangement is called post-caramelization since development of the brown color and flavor occurs after cooking. The relative contribution of Maillard browning or caramelization of sugars to color and flavor development depends on the holding temperature. Temperatures closer to 115–120 °F (239–248 °F) promote Maillard browning whereas temperatures above about 132 °C (270 °F) favor sugar caramelization (although Maillard browning also occurs at these elevated temperatures).

Numerous types of caramelizers are available, but the general principle is to provide sufficient residence time (10–20 min) at elevated temperatures, with no further water loss, to allow caramelization to occur. A caramelizer may be as simple as a large tank (heated and agitated) that provides sufficient residence time at elevated temperatures. Alternatively, a second SSHE may be used to provide the necessary residence time, with the agitation and scraping action responsible for preventing scorching of the milk ingredient on the hot surface. A heated screw conveyor may also be used to ensure adequate residence time at high temperature to promote browning.

An alternative to post-caramelization is to promote browning prior to the cooking step. Here, the candy mass is heated in a vessel (usually a SSHE) under pressure so that extremely high temperatures (320 °F) can be attained without moisture loss. The higher temperature promotes very rapid browning (see Section 10.4.1) while keeping the water in liquid form. Once sufficient brown coloration has been developed, usually within a few minutes at the most, the caramel then passes through a second cylinder to provide cooling down to 240 °F for moisture control. Upon exiting the second unit to atmospheric pressure, the moisture evaporates (flashes off) to give the desired final water content. Pre-caramelization is a rapid and efficient process; however, the caramel-type flavors generated in this process may differ (from typical batch or post-caramelization) due to the elevated temperatures and moisture contents at which the reactions occur (see Section 10.4.1). At these high temperatures, caramelization occurs very rapidly.

Once cooking and development of the caramel color and flavor have been completed, the candy mass is cooled to the desired temperatures for additional ingredient addition and forming. Additional flavors and other ingredients (e.g., nuts, chocolate liquor, seed crystals) may be added at a temperature of about 82 °C (180 °F). When seeds or fondant are added to promote graining, sufficient cooling is needed to prevent complete dissolution of the seeds.

10.3.3 Cooling and Forming

There are numerous methods for cooling and forming caramel and fudge prior to packaging. Perhaps the simplest method is to pour the cooked candy mass onto a cold table to cool to a point where the candy can be cut into the desired shapes and wrapped. The nature of the cooling and forming process depends on the end use for the caramel, from application of fluid caramel on a candy bar to formation of desired shapes for subsequent coating in chocolate.

Figure 10.5 Cooling wheel for cooling caramel (Courtesy of R. Hohberger, SPEC Engineering)

Hot caramel candy mass can be cooled on a cooling drum (Figure 10.5). The hot mass is poured onto a rotating cooling drum to decrease temperature as the drum slowly rotates. A cooling drum contains cooling fluid (cold water or some other refrigerant) inside the drum to remove heat from the caramel mass. The thin (<1 cm) layer of candy mass on the drum cools very quickly and reaches the desired temperature (40–50 °C; 104–122 °F) within the time needed for part of a revolution. Multiple cooling drums may be needed to reduce temperature to the desired level. Once the caramel mass has cooled, it is scraped off the drum and fed into the forming unit. Alternatively, the fluid caramel may be sheeted by forcing the hot, fluid mass through a set of rollers and fed onto a cooling belt or tunnel prior to use (application onto a candy bar, roping for cut and wrap machines, etc.).

In some cases, the cooked caramel mass may be directly deposited into shaped molds, whether into starch trays or starchless molds, to form the desired shapes. The cook temperature of caramel for starch depositing is generally slightly lower than normal so that it has slightly higher water content and flows readily. The low viscosity is necessary to fill the mold (no air pockets) and take the shape of the mold. With starch molding, the caramel is allowed to cool and dry overnight

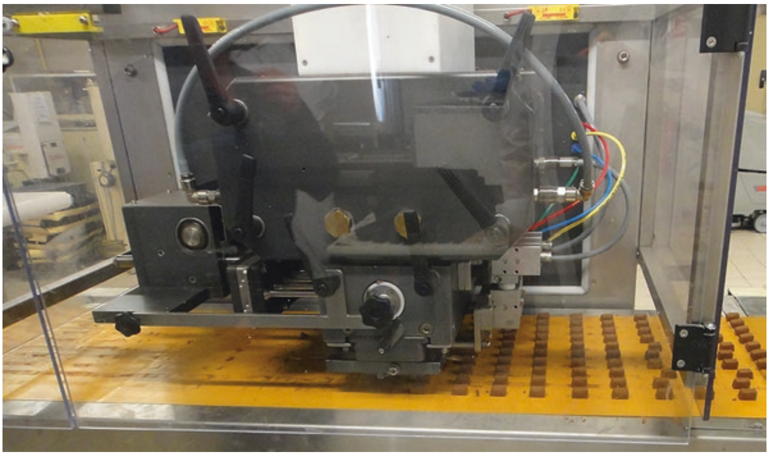

Figure 10.6 Extruder for forming and shaping caramel (Courtesy of Hacos)

in the molds prior to further processing (e.g., enrobing in chocolate). With starchless molding, slightly lower moisture content is needed during depositing since no additional drying takes place in the mold. Once the caramel has cooled, it is removed from the mold for further processing (chocolate enrobing, etc.).

Forming of caramel can be done in a variety of ways, depending on the end product. To form individually wrapped pieces of caramel, the cooled candy mass is passed through batch rollers and a candy roper/sizer, similar to the process used for hard candy (see Section 8.3.1.5), to form a cylinder or rope of plastic caramel. A cut and wrap machine is used to create the individually wrapped pieces. Warm caramel can also be sheeted through extrusion rollers onto a cooling conveyor. After the mass has cooled sufficiently, it is cut by slitter knives into long strips of caramel and then guillotined to the proper length. Problems of cutting extremely sticky caramel can be reduced by using a sonic cutter/guillotine or high pressure cutters.

Caramel mass may also be extruded to form shapes, often by cutting a piece with a wire knife onto a conveyor belt, as seen in Figure 10.6. The plastic candy mass is fed between two rollers that extrude the caramel through a die in the desired shape. Cutter blades moving back and forth immediately after the die cut the candy to the desired thickness, allowing the candy piece to be collected on the conveyor below.

For grained caramel or fudge, development of the crystalline structure may be needed prior to forming. This can be accomplished either by working the mass, as in fondant crystallization, or by adding a graining agent such as cooked fondant, fondant sugar or powdered sugar. Control of temperature is critical in either case. When crystallizing fudge by agitation, the candy mass must cool to a temperature at which the kinetics of crystallization are optimal for formation of numerous small crystals (see Section 2.2). Intense agitation (beating) at this temperature results in a fudge mass with numerous small crystals that impart a smooth, short texture. Typically, temperatures about 40–50 °C (104–122 °F) are needed to promote proper crystallization. Beating of fudge can be done by hand on a cold table or in a plough-type cream beater (see Section 9.3.1.2). Alternatively, fondant can be added to the candy mass to set the grain. Temperature of fondant addition is important since the candy must be cooled sufficiently to prevent complete dissolution of the crystals in fondant yet be warm enough to adequately mix in and disperse the fondant pieces. Temperatures on the order of 65.5–82 °C (150–180 °F) should be sufficient.

Forming of fudge may be as simple as pouring the crystallized fudge mass into containers to cool prior to cutting into slices. Fudge may also be poured into molds (usually starchless molds are used) and allowed to solidify prior to further processing. Fudge for molding is generally poured at slightly warmer temperatures (65.5–82 °C; 150–180 °F) to allow proper filling of the mold forms. Fudge may also be processed through a sheeting unit onto a cooling conveyor prior to slitting and cutting into the desired shapes.

Cooling of toffee generally involves slabbing the candy mass on a cold table or conveyor, scoring the sheet into the desired pieces, allowing the candy to cool undisturbed to reach the glassy state, and then breaking the mass into the desired candy shapes. From here, toffee pieces are typically coated or enrobed in chocolate.

10.4 Product Characteristics

Caramels, fudge and toffee are quite complex candies. Cooked dairy flavors are critical to the desired flavors and the chemical reactions during processing need to be controlled carefully to obtain a consistent product. Texture, from graining to cold flow, is governed primarily by the product microstructure. Caramel and fudge contain lipid emulsions and protein aggregates in an amorphous sugar matrix that contribute to its physical structure and attributes, whereas English toffee is an emulsion stabilized by a sugar glass.

10.4.1 Color and Flavor Generation

Probably the most important attribute of caramel, fudge and toffee is the development of the characteristic color and flavor notes. These colors and flavors are generated through a combination of two reactions, sugar caramelization and the Maillard browning reaction, although in some cases, cooked butter flavors contribute to the overall flavor. Caramelization (see Section 1.4.3.2) occurs when sugars undergo a complex series of reactions at elevated temperatures, typically above about 132 °C (270 °F). Maillard browning (see Section 1.4.3.1), also a complex series of reactions, requires both proteins and reducing sugars (i.e., glucose, fructose, lactose, etc.) as substrates. Both reactions are enhanced at elevated temperatures and produce similar flavorants and colors, although the exact flavor notes produced depend greatly on the reactants present and the conditions (temperature, pH, water content, etc.) of the reaction.

The Maillard browning reaction is named after French chemist Louis-Camille Maillard who first detailed the reaction mechanisms (Billaud and Adrian 2003). From browning of toast to browning of cheese on pizza, the Maillard browning reaction is widely observed in a variety of foods. In addition to caramel flavor, Maillard browning is also primarily responsible for the color and flavor of both chocolate and coffee, as developed in the roasting process. The differences in flavors are due primarily to the difference substrate compounds (protein and sugars) present.

As discussed in detail in Section 1.4.3.1, the Maillard browning reaction is actually a series of complex reaction steps involving proteins and reducing sugars. As one would expect for such a complex series of reactions, numerous compounds are produced in the Maillard browning reaction, each of which contributes in some way to the flavor and color. Of the compounds produced, maltol, isomaltol, HMF (hydroxymethylfurfural) and DHF (dimethylhydroxyfuranone) are important characteristic flavors that contribute to the characteristic caramel flavor. Other compounds produced from Maillard browning include dihydro dihydroxy methylpuranone, various dicarbonyls (e.g., diacetyl), polycarbonyls and aldehydes, as well as unsaturated heterocyclic compounds.

Caramelization (see Section 1.4.3.2) is a reaction involving sugars at high temperatures that does not require proteins. It starts with dehydration of the sugars to form a variety of flavor molecules, which include HMF and DHF. Both soluble and insoluble polymeric pigment compounds, such as caramelen and humin, are also produced during caramelization.

Since HMF and DHF are both formed in the Maillard browning and caramelization reactions, it is no surprise that similar caramel-type flavors arise regardless of how the caramel was cooked.

Still, the specific flavor profile of a cooked caramel depends on both process conditions like time and temperature, which affect the relative contribution of caramelization and Maillard browning, and the composition of the ingredients in the formulation. Parameters that affect both reactions include the types and amounts of reducing sugars, water content, pH, and temperature. Other parameters that can influence the nature of the Maillard browning reaction in caramel include types and amount of proteins, oxygen level, trace metal content, phosphate content, and the presence of other inhibitors.

The relative contribution of Maillard browning and sugar caramelization to the flavor of caramel depends primarily on the cooking conditions. In batch cooking of caramel, where a pre-mix is cooked directly to a temperature of 121 °C (250 °F) at the most, only Maillard browning occurs. The rate of sugar caramelization at temperatures below about 123–138 °C (270–280 °F) is negligible, so it is only when caramel is cooked above these temperatures that sugar caramelization contributes to the flavor. In the case of pre-caramelization, where browning occurs at temperature upwards of 160 °C (320 °F) and high water content, sugar caramelization contributes substantially to the caramel flavor development as does Maillard browning. For this reason, pre-caramelization and post-caramelization processes are likely to give caramels with distinctly different flavors than batch-cooked caramel.

Another important contributor to caramel flavor is that of cooked butter. Milk fat, when heated to elevated temperatures, undergoes a series of complex reactions that generates characteristics flavor compounds. These include, among others, free fatty acids, ketones and lactones. The presence of oxygen and certain metal ions (copper) during cooking contribute to the generation of these flavors. Replacement of milk fat with vegetable fats in a caramel formulation significantly reduces production of these flavor compounds, with a significant reduction in caramel flavor notes.

Table 10.2 Compounds identified in distillate of cooked milk caramel (Keeney et al. 1970)

Acids	
Acetic	Butanoic
Hexanoic	Octanoic
Nonanoic	Decanoic
Dodecanoic	Tetradecanoic
Pentadecanoic	5-methyl-2-furoric acid
Lactones	
δ-decalactone	δ-dodecalactone
δ-octalactone	
Esters	
Ethyl acetate	Furfuryl acetate
Butyl palmitate	
Alcohols	
Furfuryl alcohol	Undecanol
Aldehydes	
2-furaldehyde	Phenylacetaldehyde
B-methyl mercaptoproprionaldehyde	
Ketones	
2-pentanone	2-hexanone
2-heptanone	2-nonanone
2-decanone	2-tridecanone
2-pentadecanone	2-furyl methyl ketone
1-hydroxy-2-propanone	Acetoin
Diacetyl	

The combination of browning and lipid reactions produces an extremely complex set of chemical compounds that make up caramel flavor and color. A sampling of the range of compounds found in caramel distillates is shown in Table 10.2.

In toffee cooking, a combination of Maillard browning, sugar caramelization, and cooked butter are responsible for color and flavor development. English toffee contains primarily sucrose and butter, with typically no glucose syrup or additional milk ingredients added. Only a small amount of protein is present, arising from the aqueous phase of butter. In addition, no reducing sugars are added, so that the only reducing sugar comes from inversion of sucrose during heating. Thus, Maillard browning is probably not the primary contributor to brown color formation, with sugar caramelization dominating. However, due to the high milk fat content (≈30%), cooked butter flavor plays a significant role in the flavor profile of English toffee.

10.4.2 Microstructure

The physical attributes of caramel, fudge and toffee are related to the different microstructures that are produced. In particular, physical characteristics of importance include firmness (hardness), stickiness, cold flow (the ability to flow at room temperature), and short texture. These physical attributes are generally related to water content, the nature of the fat emulsion and protein network, and the presence (or absence) of sugar (sucrose, lactose) crystals. Temperature also plays a role in determining the physical properties of these candies. In all cases, an increase in temperature causes the confection to get softer and ultimately to flow.

10.4.2.1 Caramel

Ungrained caramel is an aqueous solution that contains dissolved sugars (sucrose, glucose syrup, lactose), salts and proteins (Heathcock 1985) with water content dependent on the cooking temperature. Fat globules, protein aggregates and sugar crystals (in grained caramel) also contribute to caramel microstructure. Each component can influence the physical properties of the finished product.

The physical characteristics of caramel are determined to a large extent by the amorphous nature of the sugar phase, which is influenced in part by the water content, the nature of the proteins in the matrix, and the particular combination of sugars in the finished product. Controlling characteristics of the amorphous sugar matrix is critical to making caramel with the desired properties. With everything else being the same, caramel with higher water content is more fluid, with a low T_g (see Section 2.9), even to the point of being runny if water content exceeds about 15%. A soft caramel with over 10% water might have a T_g as low as −20 to −30 °C (−4 to −22 °F). Chung et al. (1999) indicated that glass transition in caramel occurred between −12.3 and −26.3 °C (10 and −15 °F) while Ahmed et al. (2006) found the mid-point of the glass transition was between −14 and −28 °C (7 to −18 °C). Differences between the two studies were most likely due to differences in water content and formulation of the finished caramel. Caramel cooked to low water content (<5%) behaves more like a hard candy, with the amorphous sugar matrix being in a glassy state. In such a caramel, T_g should be well above room temperature, resulting in a hard, brittle candy. Stickiness and cold flow are directly related to water content and temperature, all else being the same. That is, higher water content and/or higher temperature generally indicates a stickier caramel that is more prone to cold flow.

Table 10.3 Glass transition temperatures of caramels made with different dextrose equivalent (DE) glucose syrups (Foegeding and Steiner 2002) cooked to the same temperature (119 °C; 246 °F)

Sweetener	T_g (°C/°F)	Water content (%)
26 DE	20 (68)	8.4
42 DE	9 (48.2)	–[a]
62 DE	5 (41)	–[a]
High fructose 55	0 (32)	9.6

[a] Not measured

Along with water content, the sugar profile in the finished product influences the T_g of caramel, which subsequently determines properties like firmness. All else being equal, higher content of lower molecular weight sugars in the finished caramel leads to softer product with a lower T_g. For example, caramel made with glucose syrup of decreasing average molecular weight (increasing DE – Dextrose Equivalent) results in softer (less firm) caramel due to the reduction in T_g, as shown in Table 10.3. In similar manner, caramel that contains higher invert sugar than normal will have a lower T_g and be a softer caramel. In general, it is widely accepted that caramel is increasingly sticky when made with higher levels of low molecular weight sugars (invert sugar or higher DE glucose syrup). However, stickiness depends to some extent on the method of measurement and in particular, on the type of surface used for evaluating sticking. Caramel may have different behavior when in contact with plastic packaging as compared to stainless steel equipment or tooth enamel. Further, stickiness in the mouth is most likely influenced by salivation, which dissolves the caramel matrix and changes adhesive behavior. Caramels made with greater content of low molecular weight sugars are also more prone to cold flow.

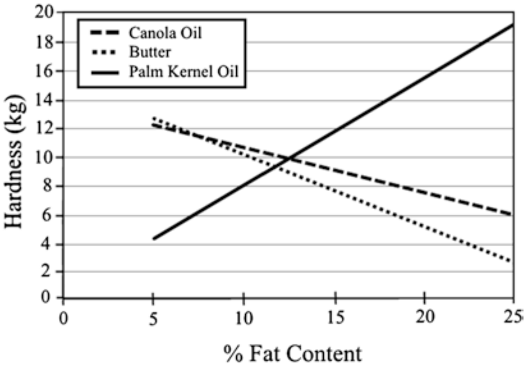

Figure 10.7 Effects of fat content and type on hardness of caramel (From Bulchuk and Hartel, unpublished)

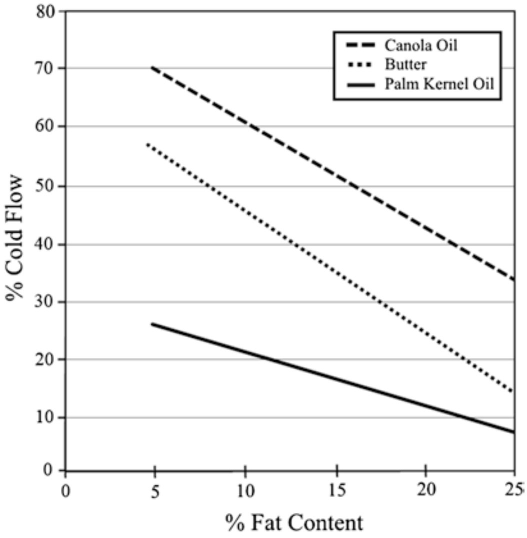

Figure 10.8 Effects of fat content and type on cold flow of caramel (From Bulchuk and Hartel, unpublished)

Caramel contains anywhere from 8% to 20% fat, which not only influences caramel flavor, but also impacts physical properties. The fat is dispersed throughout the continuous sugar matrix in the form of numerous small fat globules, with size depending on the method of homogenization. High-shear homogenization leads to fat globules about 1–10 μm in diameter. These fat globules are semi-crystalline, meaning that a portion of the fat is crystalline yet some still remains in liquid form. The solid fat content (see Section 4.3.2.2.1) within each globule depends primarily on the nature of the fat used (milk fat, vegetable fat, etc.) and its inherent solid fat profile (solid fat as function of temperature). The amount of fat and its level of solid fat content have an important impact on physical properties (Mendenhall and Hartel 2016b). Figure 10.7 shows the effects of fat content and type on hardness of caramel (as measured by penetration force and sensory evaluation). The effects of increasing fat content on hardness depend on the solid fat content of the fat. An increase in the level of hardened vegetable fat (solid fat content of 46% at 25 °C/77 °F) caused an increase in hardness of the caramel, whereas butter (solid fat content of 10.5% and canola oil (0% solid fat at 25 °C) caused the caramel to be softer. As a filler in the amorphous matrix, the hardness of the fat droplets had a significant effect on hardness of the caramel, but the effect was dependent on the hardness of the fat globule itself. Figure 10.8 shows the effects of the same fats on cold flow (as measured by spread of a caramel disc over time) of caramel. In this case, an increased fat content resulted in a decrease in cold flow regardless of the solid fat content of the droplet (Mendenhall and Hartel 2014). Use of liquid oil is generally undesirable in caramel since the resulting product would be softer and undergo cold flow, as well as feeling greasier due to oil separation. Also, the emulsion droplets moderate the stretchiness of caramel to some extent, but because the fat is semi-crystalline and not completely solidified, the droplets also can be deformed (Mendenhall and Hartel 2014). Thus, the fat emulsion does not impart as much of a short texture as sugar crystals.

Fat is known to moderate the stickiness of confections (Mendenhall and Hartel 2014). A recent study by Morton et al. (2003) used Atomic Force Microscopy (AFM) to characterize the surface of a caramel to verify that there are indeed surface structures that were attributed to the fat phase. The mechanism then for fat reducing stickiness may be as simple as they replace some of the sugars at the surface and reduce the surface forces between the caramel and either teeth or processing equipment. The presence of fat globules at the surface also reduces the surface area for moisture sorption, decreasing the apparent hygroscopicity of the caramel. Fat globules at the surface also explain the differences in caramel color between caramels made with different fats (Mendenhall and Hartel 2016b). The differences in caramel color tracked directly with the differences in the colors of the fats used (vegetable fat, milk fat and canola oil).

Caramel typically contains between 1% and 4% protein from milk. There are actually numerous proteins in milk, although caseins make up the largest part (80%) with the whey proteins, α-lactalbumin and β-lactoglobulin, making up most of the remaining 20%. Due to the presence of both hydrophobic and hydrophilic regions, caseins form micellar structures in solution. Whey proteins, in globular form, are dissolved in the aqueous phase. In caramels, the proteins form an aggregated matrix around the fat globules during cooking. The aggregated protein structure contributes to the physical characteristics of the continuous phase of caramel and, in particular, is responsible for the stand-up characteristics (or resistance to cold flow).

The proteins in caramel, including the amount and type, clearly play a critical role in determining the physical properties (Mendenhall and Hartel 2014, 2016a; Eberle et al. 2016). An increase in protein content, all else being the same in caramel, causes an increase in hardness and a decrease in cold flow. Higher protein content also reduces the stickiness of the caramel (Mendenhall and Hartel 2016a).

Further, it is widely recognized, although poorly understood, that changes in the nature of the proteins during production of sweetened condensed milk or evaporated milk can have a significant impact on the textural aspects of caramel. Changes in the nature of the proteins due to processing of the dairy ingredient are suspected as the primary cause for variability in caramel texture. Similarly, it has been shown that forewarming treatments have a significant effect on caramel texture (Attapatu 1997; Mendenhall and Hartel 2016a). Denatured whey proteins formed during forewarming interact with casein micelles and inhibit their ability to form an aggregated network around fat globules. The end result is a softer caramel (Mendenhall and Hartel 2016a), although there was no effect on cold flow.

The pH of a caramel pre-mix also influences the proteins in caramel during cooking. Specifically, if pH of the milk component is too low, protein aggregation occurs, imparting a grainy, lumpy texture to the caramel as it cooks. Protein graining is easily differentiated from sugar graining by the tapioca-like texture that results from protein graining. Protein graining is likely the result of a combination of effects, including casein aggregation as the pH is reduced and whey protein denaturation during cooking. Buffering or emulsifying salts, such as baking soda, disodium phosphate, and sodium citrate, may be used to reduce the protein graining, possibly by simply moderating pH to minimize aggregation (Eberle et al. 2016). However, some salts also influence the Ca ion partitioning between micelle and solution, thereby influencing the nature of the casein micelle and its propensity to aggregate.

10.4.2.2 Grained Caramel and Fudge

Although the range of water content in fudge is generally narrower than that found in caramel, the fat globule and protein structures in fudge are similar to those of caramels. It is the presence of sugar crystals that gives grained caramel and fudges their unique, short texture. The numerous small crystals in grained caramel and fudge break the continuous network of protein and carbohydrate, leading to the short texture. The amount and size of sugar crystals determines the extent of this short texture characteristic.

The amount of sugar crystalline phase determines the effect on textural properties. An increase in sugar crystal content caused a decrease in hardness in caramel model systems, up to a point (Miller and Hartel 2015). Once crystal content reached about 35%, no further decrease in hardness was observed. A similar response was observed for cold flow, with less cold flow as crystal content increased to about 35%, after which there were no further changes in cold flow. In commercial grained caramels, a relatively small (less than 10%) amount of crystalline sugar provides some degree of shortness, similar to that found in a chewy candy. Because the crystal content is low, grained caramels still retain much of their chewy texture, with only a slight change in texture. In fudge, however, the higher degree of crystallinity gives a shorter, softer, sometimes almost crumbly, texture.

Crystal size in grained caramel and fudge affects texture, but probably is most important in terms of sensory perception. For the most part, crystals smaller than about 15 μm are desired in grained caramel to minimize the grainy sensory perception. When the crystals in either caramel or fudge exceed about 20 μm, they are detected on the palate and impart a coarse texture. In fudge, this coarse texture is sometimes desirable. Typically, fudge that is seeded through addition of fondant has grainier texture than that made by agitation to induce crystallization.

10.4.2.3 Toffee

Toffee is somewhat distinct from caramel and fudge in that very little (if any) corn syrup or milk is added. Sucrose and butter are the two main ingredients in the American version of English toffee (in England, toffee refers to a hard ungrained caramel with moisture content about 6%). With the only doctor to control crystallization being whatever invert sugar is formed during cooking, a cooked toffee mass is prone to sugar crystallization and must be handled gently to prevent crystallization. Excessive inversion results in a very hygroscopic product that easily picks up moisture, becomes sticky and potentially grains.

The microstructure of toffee is closer to that of a hard candy than either caramel or fudge. The low water content results in a glassy sugar matrix throughout which the lipid emulsion is dispersed. The fat globules, semi-crystalline in nature, disrupt the glassy sugar matrix and give toffee a more friable texture than a normal hard candy. A well-made toffee should break easily on the teeth, with little stickiness of the candy pieces in the mouth during mastication. Addition of nut pieces also helps provide the desired texture.

In English toffee, the high butter content (≈40%) means that production of a stable emulsion is extremely critical. Lecithin, added at the beginning of the cook, is often used to help produce a smooth emulsion with small fat globules. However, excess agitation during processing can induce coalescence of the liquid droplets, resulting in oiling out of the butter. This appears as an unsightly layer of liquid fat on top of the cooking candy mass. Sufficient agitation is needed to prevent scorching and maintain the batch, but too much agitation has negative consequences on emulsion stability. Excessive handling of the toffee mass as it is cooling should be minimized to prevent oiling off. Once the candy mass is cooled to room temperature, the fat globules become partially crystalline and the sugar phase has high viscosity, so coalescence is no longer a concern.

10.4.3 Shelf Life

The factors that affect stability of caramel, fudge and toffee may be different, generally dependent on the water, sugar, and fat content. Since these candies contain fat, lipid oxidation may be a concern for long-term exposure. Water migration, either into the candy to cause stickiness or out of the candy to cause drying out, may also limit shelf life. In ungrained caramels, crystallization of sugar (sucrose or lactose) during storage may cause sufficient changes in texture to signal end of shelf life. Graining of sugar may also signal the end of shelf life of toffee. Proper formulation and storage conditions can be used to mitigate the effects of each of these potential spoilage mechanisms.

10.4.3.1 Lipid Oxidation

One potential problem that can occur during storage of caramel, fudge and toffee is off-flavor development due to lipid oxidation, especially if milk fat is used. Exposure to oxygen causes rapid rancid flavor development due to lipid oxidation (see Section 4.2.3). This is particularly true if a copper kettle was used for cooking since metal ions, particularly Cu, are known to catalyze lipid oxidation. The high fat content of toffee means that it is especially prone to lipid oxidation when exposed to oxygen in air.

Of particular concern for rancid off-flavor development are unsaturated fatty acids, which are most easily oxidized. Vegetable fats are significantly more resistant to oxidation than milk fat because they contain less unsaturated fat (and have no short-chain fatty acids). If nuts are used in caramel, fudge and toffee, the highly unsaturated nut oils present may exacerbate oxidative rancidity. Butter, in particular, is prone to oxidative rancidity, because of the high content of short-chain fatty acids. Fatty acids like butyric acid (four carbon chain) and caproic (six carbon chain) have particularly noxious odors at very low threshold levels so that even slight oxidation of milk fat can cause significant rancid off-flavors.

Lipid oxidation can be controlled in several ways. Cool storage conditions, even freezing, can extend shelf life. For each 10 °C (18 °F) lower storage temperature below room temperature, shelf life is extended by about two times. Displacing the oxygen in the package head space and packaging in a hermetically sealed environment also extends shelf life, as does completely enclosing the candy in a chocolate coating. Finally, antioxidants (BHA, BHT, TBHQ, tocopherols, etc.) may be added to the fat portion of the formulation to inhibit lipid oxidation.

10.4.3.2 Moisture Migration

One of the main problems associated with storage of caramel, fudge and toffee is moisture gain or loss. The water activity of caramels falls in a very broad range of about 0.3–0.6 (or even higher for liquid caramels), depending on moisture content and formulation. Storage in humid environmental conditions may result in moisture sorption and stickiness. To minimize problems of moisture sorption, caramel should be made with less than 4% invert sugar, whether that comes from direct addition of invert sugar in the formulation or from inversion during cooking. Processing at conditions of high relative humidity should be avoided and to prevent moisture sorption during shelf life, proper packaging (adequate moisture barrier) is needed. English toffee, a sugar glass, is particularly prone to moisture sorption, in the same manner as hard candies. With a water activity of 0.2–0.3, toffee must be protected from environmental moisture to protect against moisture uptake and stickiness.

Some caramels, particularly those with higher water content, have sufficiently high water activity that they lose moisture to the air during storage and dry out. Particularly in colder, northern climates and dry desert environments, moisture migration from the candy to the dry air causes caramel to harden over time. Even when double wrapped (individually wrapped candy in an overwrap bag), moisture loss occurs slowly over time.

Fudge generally has a water activity a little higher than caramel, so it is more likely to experience moisture loss during storage. In the same way as soft caramels (high moisture content) dry out, fudge also tends to get harder over time until the texture becomes too firm and crumbly. To retard moisture loss and extend shelf life, using a good package material (moisture barrier with good seals) is essential although formulations that include humectants can minimize the driving force for moisture loss.

In both caramel and fudge, dry inclusions (nuts, crisps, etc.) can experience moisture migration issues over time. Textural changes that occur as moisture moves from the caramel (becomes firmer) to the inclusion (becomes soft or soggy), can signal the end of shelf life of these products. Use of nuts with lipases could also promote hydrolytic rancidity.

10.4.3.3 Graining

Graining during storage may limit the shelf life of some ungrained caramels and toffee. If an ungrained caramel is formulated with excess sucrose or lactose content, it is prone to crystallization of the sugars during storage. In general, the principles of controlling sugar crystallization discussed in Section 2.10 apply to caramel and fudge; however, the lack of certainty in the sucrose solubility curve in these complex formulations makes it difficult to use the fundamental approach. Thus, more empirical approaches, such as the ratio of sucrose to glucose syrup, are used to understand and control graining during storage of caramel.

For example, if the sucrose to glucose syrup ratio is too high, the amorphous sugar phase of caramel may be sufficiently supersaturated with respect to sucrose to crystallize during storage. Graining is a kinetic response to supersaturation, meaning that the time needed for crystals to form depends on the magnitude of the supersaturation. Generally speaking, if there are more sucrose solids than syrup solids in the formulation, supersaturation is high and there is insufficient inhibition to delay onset of crystallization, so that graining occurs rapidly, perhaps even during processing. On the other hand, when there is more glucose syrup than sucrose (ratio of sucrose to glucose syrup <1), there is sufficient inhibition of crystallization and graining is unlikely to occur. A wide variety of caramel formulations fall between these two cases, with the time required for onset of crystallization decreasing as the sucrose to glucose syrup goes up.

Figure 10.9 shows how the induction time for graining of caramel changes as the ratio of sucrose to glucose syrup changes (Lenz and Hartel 2005). At very high ratios of sucrose glucose syrup (S/CS), the induction is rapid (unstable product) and at very low ratios (more glucose syrup than sucrose), the induction time is very long (relatively stable product). At intermediate ratios, the water content appears to play an important role in induction time, with higher water content leading to faster nucleation. Figure 10.10 shows the effects of the ratio of sucrose to water (S/W) on graining. Similar to the ratio of sucrose to glucose syrup, there are three regions. High S/W gives rapid nucleation (unstable), whereas low S/W gives very slow nucleation (relatively stable to graining because of the reduced molecular mobility near the glass transition). At intermediate ratios, the glucose syrup content factors into graining, with higher S/CS inhibiting nucleation as expected.

Graining is particularly a problem in caramels formulated with whey components since the solubility of lactose is quite low (16%) at room temperature. Whey solids generally contain over 65% lactose, so addition of high levels of whey may require reformulation to reduce the content of lactose to prevent graining during storage. Some suggest that lactose level should be less than 17% in a caramel formulation to ensure that graining does not occur.

Graining of English toffee may also be a concern in shelf life. Since toffee is a sugar glass, the same issues of moisture uptake and graining apply as discussed previously for hard candies (see Section 8.4.3.2). In the case of toffee, the potential for graining is even higher than in hard candy because there are no doctors added to the batch to control crystallization. The only doctors present would be the invert sugar formed during cooking. In batch cooking, perhaps 5% of the sucrose is inverted, depending on the speed of cooking, meaning that there is very little protection against graining for English toffee other than the inhibited molecular mobility due to the glass state. Lipid oxidation occurs more rapidly than graining in toffee so recrystallization is rarely the mechanism for end of shelf life.

10.4.3.4 Microbial Growth

Caramel and toffee generally do not have microbial issues due to the low water activity. However, some soft, fluid caramels may have water activity higher than 0.68, suggesting the potential for yeast and mold growth over time.

Due to the crystalline nature of fudge, there is a potential at times for it to support mold growth, especially if some condensation occurs on the surface of the product or the packaging. If fudge is made during the summer in high humidity and cooled to below the dew point in a refrigerated room, water droplets condensing on the surface can dissolve sugar crystals and provide an opportune environment for microbial growth. Mold spots on fudge can be prevented by using dehumidifiers in the process area to prevent condensation or by addition of a small amount (0.1%) of a microbial inhibitor like potassium sorbate (note that pH must be <6.5 for potassium sorbate to be effective). To help prevent condensation and mold growth, fudge should be cooled to room temperature prior to packaging.

10.5 Troubleshooting

Caramel, fudge and toffee are quite complex confections and even with the most careful attention, problems can arise (Cooke 2003). Some of the main problems include cold flow, graining, and candy that is too sticky or too hard.

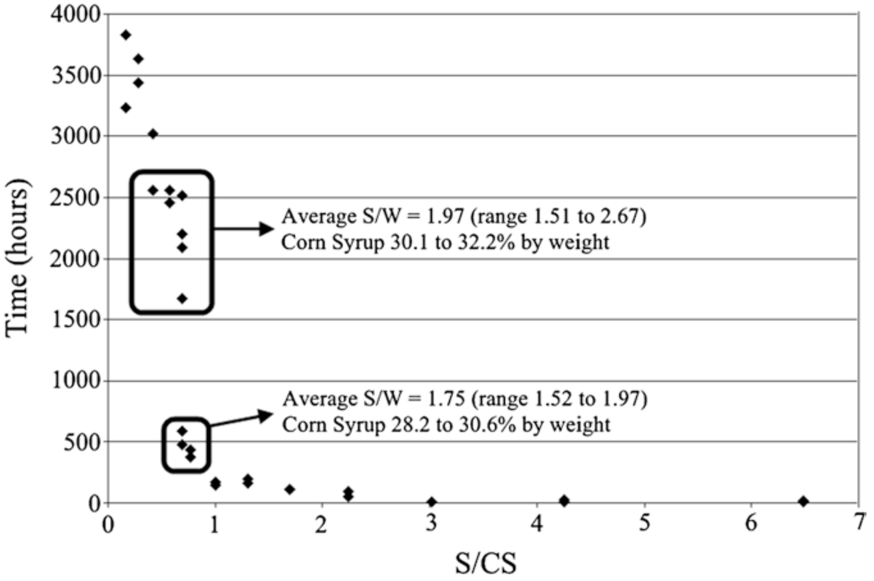

Figure 10.9 Effects of ratio of sucrose (S) to glucose syrup (CS) content on induction time for graining of caramel, at different levels of water (W) (From Lenz and Hartel 2002)

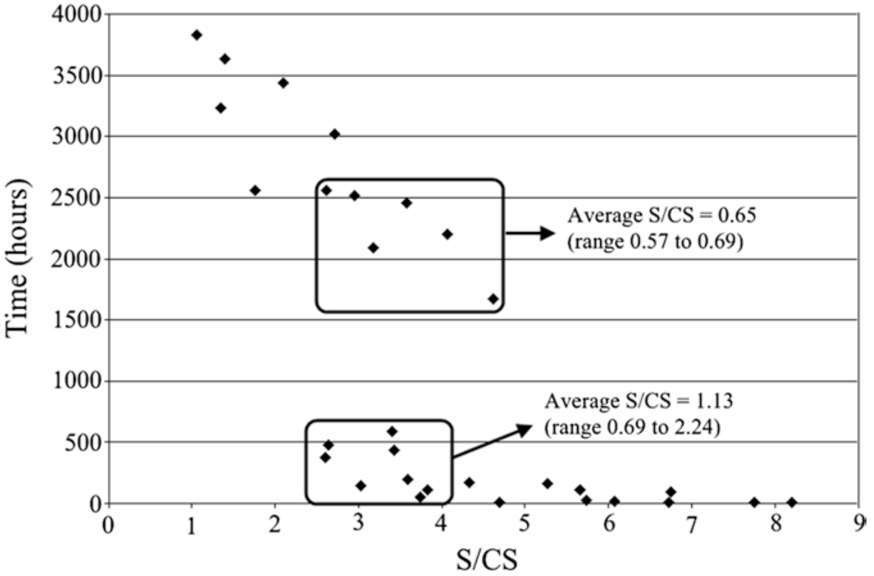

Figure 10.10 Effects of ratio of sucrose (S) to water (W) content on induction time for graining of caramel, at different levels of glucose syrup (CS) (From Lenz and Hartel 2002)

10.5.1 Cold Flow

Cold flow is defined as the ability of a semi-solid mass to flow under its own weight (gravity) even at low (room) temperature. It is a particular problem in caramels (as well as taffy and some other chewy-type candies). If a candy exhibits flow even after it is formed, there is the potential for that flow to change the shape of the candy. Instead of, for example, a caramel with a perfect cube shape, the edges may flow to fill whatever container or shape holds the candy pieces.

To understand cold flow in caramels, it is important to understand the effects of temperature and molecular interactions on viscosity as well as the effects of structural elements (fat globules, sugar crystals, etc.) on the properties of the matrix. In a sugar mass, viscosity increases as temperature is lowered and as concentration of sugars in solution increases/water content decreases (see Section 2.2). The molecular interactions among sugar molecules (e.g., hydrogen bonding) increase as temperature goes down and concentration goes up, resulting in this increase in viscosity. If temperature is decreased and/or concentration increased, the sugar syrup becomes amorphous and eventually undergoes a glass transition. The same phenomena occur in a caramel sugar syrup, except the addition of proteins enhances the extent of inter-molecular interactions. The protein matrix causes a substantial increase in viscosity compared to a sugar syrup of the same concentration. The protein also causes the candy mass to have viscoelastic behavior.

Thus, a caramel candy mass has sufficiently high viscosity at temperatures on the order of 100–120 °F that it can withstand the force of gravity, at least for a short period of time. This allows the caramel to be formed, into a cube for example, and to retain its shape for a long enough time that it can be cooled to room temperature without deforming. In some cases, however, the candy mass may not have the proper viscoelastic properties and it will be prone to cold flow.

Factors that affect cold flow then include water content, extent of graining, fat type and content, protein type and content, and emulsifier use, all of which influence the viscoelastic properties of caramel. If cold flow is a problem, options include:

- Lowering moisture content: Less water means more viscous continuous phase, which is more resistant to flow and deformation.
- Increasing fat content or decreasing fat globule size: More and smaller fat globules (higher homogenization pressures) provide resistance to deformation.
- Increasing solid fat content of fat globules: Harder fat globules provide more resistance to deformation.
- Increase sugar crystal content: Sugar crystals, whether sucrose or lactose, prevent deformation, although will also reduce extensibility (enhance shortness).
- Increase protein content or protein aggregation: Higher protein content, particularly of casein micelles, inhibit deformation and reduce cold flow. Increased protein aggregation can also reduce cold flow.
- Increase emulsifier level: An excess of emulsifier content needed to coat the fat globule interface results in micellar formation, which provide structure to reduce deformation and inhibit cold flow.

10.5.2 Stickiness

In stickiness, both adhesive and cohesive forces are important. Adhesive forces are those that occur between two materials, like caramel and another surface (wrapper, tooth, equipment), whereas cohesive forces are those within the caramel itself. The balance between adhesive and cohesive forces often determines whether a material is considered to be sticky. When the caramel pulls away from the surface, if the break is caused by adhesive failure, there will be no caramel left on the probe. If there is cohesive failure, some of the caramel remains on the probe as a residue. Evaluation of stickiness is a combination of residue left on the probe surface and the amount of force needed to pull the caramel off the surface.

The nature of the surface used to probe stickiness of caramel influences the measurement of stickiness. Analytical measures of stickiness typically measure the force needed to pull a probe away from a surface, but the forces between the probe and the candy depend on the nature of the probe surface. Thus, plastic wrapping material may behave differently than a stainless steel probe in stickiness measurements, and both results may differ from sensory measures of stickiness where people are asked to chew a piece of candy and rate stickiness to the teeth (enamel coating). Sensory analysis of caramel stickiness is further confounded by the release of saliva during chewing, which can affect different sugars in different ways. In general, however, stickiness of caramel is a function of water content, low molecular weight sugars, and fat content.

Typically, as water content of a caramel decreases, its stickiness also decreases, due in part to the increase in glass transition temperature, T_g, of the mass. In general, amorphous sugars undergo a transition from sticky to leathery to glassy as their T_g increases (moisture content decreases). It has been shown that the sticky zone of amorphous sugars occurs at a temperature about 10 °C higher than T_g at a given water content, where viscosity is about 10^8 Pa-s (Downton et al. 1982). Thus, sufficiently low water content is needed to increase T_g of a caramel mass to the point where the surface is beyond the sticky point. Of course, temperature of the caramel mass also is important, with higher temperatures leading to increased stickiness.

In the same manner as increasing water content, decreasing the average molecular weight of sugars in the caramel mass also affects T_g, viscosity and stickiness. Typically, caramel made with high content of low molecular weight sugars has a higher risk of stickiness. Reformulating to replace high DE glucose syrups with lower DE glucose syrups can help prevent stickiness. If too much inversion of the sugar syrup occurs during cooking, this also can lead to increased stickiness of the finished product. Minimizing the amount of low molecular weight sugars will also help minimize moisture sorption, another cause of stickiness in caramels and toffee.

The presence of fat globules distributed throughout the caramel mass can help decrease stickiness; thus, a minimum fat content is typically needed to reduce stickiness of caramel. Even as little as 0.5% fat has been shown to significantly reduce stickiness of a sugar mass (Foegeding and Steiner 2002), both on equipment surfaces and on teeth during chewing. The theory for this is that fat globules exposed at the surface reduce the area of contact with the amorphous sugar and decrease stickiness.

Certain emulsifiers, particularly glycerol monostearate and other mono- and diglycerides, may also be added to reduce stickiness. The hydrophilic components of these molecules interact with the available water to reduce stickiness.

10.5.3 Hardness

Hardness or firmness is influenced by water content, sugar profile, protein type and content, and emulsifier type and content. As noted previously, increased water content causes a reduction in T_g and softer caramel. Water content in caramel can be influenced by cook temperature and pressure. Often a caramel that is too hard has been inadvertently cooked to a higher temperature or the hot sugar mass has been held too long at elevated temperatures such that additional moisture evaporation has taken place. Also, based on boiling point elevation principles (see Section 2.7) slightly lower ambient pressure than usual during atmospheric cooking can lead to a slight decrease in water content even when cook temperature is accurate.

Other factors that influence hardness of caramel are corn syrup levels that are too high and the increased use of proteins. Also, use of a fat with high melting point and/or high solid fat content at room temperature also leads to hard caramel.

10.5.4 Oil Separation

Oil separation from the sugar mass may be a problem in caramel or fudge if fat content is higher than 20%, and may be a problem in toffee if fat content is >40%. Separation during processing is usually a result of over-agitation (especially at cooler temperatures) and/or lack of emulsifier, which allows the liquid fat droplets to come together, coalesce and eventually separate from the aqueous sugar mass. Thus, to prevent oil separation in toffee, careful agitation is required with sufficient lecithin added to fully emulsify the fat.

10.5.5 Sugar Graining

Crystallization of sugars during shelf life of caramels was discussed in Section 10.4.3.3. Typically, proper formulation is necessary to provide sufficient inhibition of sugar crystallization or graining during processing and storage of caramels.

Other potential causes of undesired graining in caramels should also be noted. Excessive agitation, pumping and handling of warm caramel, particularly with higher sucrose to glucose syrup ratio, can induce sugar crystallization. If graining is undesired, gentle handling is always recommended. Graining can also occur if intact crystals make it through the cook process. In this case, seed crystals would be introduced to the supersaturated aqueous phase, reducing the need for nucleation and promoting rapid graining. Finally, if chocolate-coated caramel is to be reworked into a batch, it is imperative that sugar crystals in the chocolate be completely dissolved. Sufficient time at elevated temperature in the presence of sufficient water (at least 20% in the pre-mix) is needed to ensure complete dissolution. Addition of seed materials after cooking or without adequate water and time for complete dissolution effectively seeds the batch and ensures graining will occur.

In fudge, where graining is desired, control of the crystallization process is critical to obtaining the proper product texture. Similar to graining of fondant, crystallization of sugar crystals in fudge must be initiated at the proper temperature to attain the smallest sugar crystals for the finest texture. The cooked batch must be cooled statically to the optimal crystallization temperature to insure production of numerous small crystals to impart the desired smooth texture.

When fudge is seeded with fondant, coarse crystalline structure and mottled appearance is usually the result of adding the fondant at too warm a temperature. If the fondant is added to the fudge batch above temperatures of about 75 °C (≈170 °F), many of the fondant crystals dissolve. When the batch is subsequently cooled, there are insufficient numbers of seed crystals to fully grain the batch, allowing the remaining crystals to grow large and give a coarse texture. The rearrangement of the matrix as these large crystals form also causes a mottled appearance.

10.5.6 Protein Graining

The tapioca-type texture that appears in certain caramels is called protein grain. It is caused by excess protein aggregation during caramel cooking. As noted in Section 10.4.2.1, numerous changes occur in dairy proteins as they are cooked, including denaturation of whey proteins, changes in the calcium balance in casein micelles, and ultimately, aggregation between whey proteins and casein micelles. Protein graining is generally enhanced by high protein content, rapid cooking or low pH of the pre-mix.

If protein graining is a problem, there are several options to evaluate to solve the problem. First, protein content could be reduced in the formulation to reduce the extent of protein aggregation. Another option is to provide more time for the proteins to rearrange before cooking to final moisture content. This is most easily done through a forewarming step, where the pre-mix is held for a short time at 80–90 °C (176–194 °F) prior to boiling out. Alternatively, one of a variety of salts (baking soda, disodium phosphate, etc.) can be added to help neutralize the pH and reduce protein aggregation. However, caramel texture and color/flavor may be adversely affected, depending on the choice of salt used.

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Appendix

Table A.10.1 Typical composition of dairy products

Dairy product	Water (%)	Fat (%)	Protein (%)	Lactose (%)	Ash (%)	Added sugar (%)
Cream	55.0–58.0	36.0–40.0	2.0–2.8	2.8–3.0	0.4–0.6	0
Sweetened condensed whole milk	27.0–28.0	8.3–8.7	7.2–7.9	10.5–11.0	1.25–1.75	42.0–45.0
Sweetened condensed skim milk	28.0–30.0	0.3–0.5	10.0–10.5	15.0–16.2	1.75–2.25	45.0–48.0
Evaporated milk	70.0–74.0	7.6–7.8	6.8–7.2	10.0–11.0	1.25–1.75	0
Dried whole milk	2.0–2.5	26.5–28.0	25.8–26.3	38.0–38.4	5.0–7.0	0
Nonfat dried milk	3.0–3.2	0.5–1.0	36.1–37.5	50.5–52.0	7.5–9.5	0
Butter (salted)	15.5–16.5	80.0–81.0	0.2–0.6	0.4–1.0	2.0–2.5[a]	0
Butter (unsalted)	15.5–17.0	80.0–82.0	0.2–0.6	0.4–1.0	0.05–0.15	0
Whey (dried)	2.5–3.5	0.5–1.0	13.0–14.0	73.0–76.0	8.0–9.0	0
Demineralized whey (dried)	2.5–3.5	0.5–1.0	13.0–16.0	78.0–83.0	1.0–5.0	0

[a] Contains about 2% NaCl plus dairy minerals

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11 Aerated Confections

11.1 Introduction

The class of aerated confections encompasses a wide range of candy, from the highly aerated marshmallow to the lightly aerated (dense) taffy. Nougat, sponge candy and fruit chews are also found in the category of aerated candies. Aeration is also used to modify texture of other candy categories, including hard candy, brittles, and chocolate. Various types of aerated confections, categorized according to their typical density, or specific gravity, are seen in Table 11.1.

Specific gravity is the relative weight of a specific volume of candy compared to the weight of the same volume of water. One gram of water at 4 °C (37 °F) occupies 1 cm^3 of volume. One gram of aerated candy typically occupies a much greater volume, although several factors can affect specific gravity. Specifically, the nature of the dissolved solids (sugars, proteins, etc.) and the presence of particulates (emulsion droplets, inclusions, etc.) can affect density over and above the air phase. Due to the dissolved sugars, typical unaerated candy syrups may have specific gravity of 1.2–1.5, depending on solids concentration. Aeration causes a significant reduction in specific gravity, to as low as 0.2 in some highly aerated confections, and a subsequent increase in volume. Specific gravity may be measured by simply comparing the weight of a known volume of candy to the weight of the same volume of water. A simple way to estimate specific gravity is to weigh a cup filled with the aerated confection (completely filled so there are no air pockets, but without packing) and divide by the weight of the same cup filled with water.

The main ingredient that characterizes aerated confections is, of course, air. The continuous phase of the candy contains dissolved sugar (among other ingredients), but the presence of small air cells distributed throughout the sugar phase gives a unique texture and appearance to aerated candies. In addition to increasing volume (and lowering density), aeration causes an increase in the viscosity and a decrease in fluidity of the candy mass during processing and, ultimately, modifies the appearance, texture and sensory properties of the finished product. Finely dispersed air cells give a somewhat short texture, similar to that imparted by sugar crystals although not nearly as profound. Air also leads to a reduction of stickiness and cold flow, a lighter mouthfeel, a decrease in sweetness, and a lightening of color.

In order to stabilize air cells in confections, a stabilizing agent (i.e., gelatin, soy protein, dairy protein or egg albumin) is typically used. The presence of these stabilizing proteins during aeration promotes formation of bubbles and prevents their coalescence. The result is a foam made of finely dispersed air bubbles within a sugar candy matrix (the continuous phase). Other stabilizing agents include modified starches, gum arabic, agar, and alginates. Each stabilizing agent imparts

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Table 11.1 Approximate densities and water contents of typical aerated confections

Candy type	Approximate density (g/mL)	Water content (%)
Taffy	0.9–1.1	7–13
Fruit chews	0.9–1.1	5–7.5
Nougat	0.8–1.0	8–11
Marshmallow		5–18
Extruded	0.25–0.35	
Deposited	0.5–0.7	
Grained		5–10
Ungrained		15–18
Frappé	0.2–0.4	20–25
Vacuum puffed[a]	0.8–0.9	1–2

[a] Malted milk balls

a unique characteristic texture to the confection (for example, the elastic nature of marshmallow is due to the characteristics of gelatin).

Formation of all aerated candies generally follows the same process, although some differences exist for the different types. First, the sugar mass that forms the continuous phase is mixed and cooked to the desired water content. Typically, the stabilizing agent is added after the sugar mass has cooled slightly since denaturation and/or degradation of the proteins used as stabilizing agent can occur if temperature is too high. Numerous aeration technologies exist; aerated confections can be extruded with air injection, whipped in mixing bowls, pulled on taffy hooks, or aerated chemically. The viscosity during aeration and the intensity of agitation determine the nature of the air cells (e.g., bubble size distribution). For certain stabilizers (e.g., gelatin), temperature control is also important to ensure proper solidification. Following aeration, additional ingredients may be added to give the desired color, flavor, and texture. Forming candies from the aerated mass can be done (1) by depositing either in starch or plastic molds, (2) by extrusion through a forming die, (3) in batch rollers to form ropes of candy that are formed and cut into the desired shape, or (4) spreading the candy mass into a sheet for scoring and cutting. A few candies, like malted milk balls and some puffed hard candies, are aerated through vacuum expansion.

The texture of aerated confections is governed to a large extent by the air phase, although the nature of the continuous sugar phase also imparts certain characteristics. Taffy and ungrained marshmallow contain higher amounts of glucose syrup than sucrose, so the sugar all remains in the liquid (or amorphous) state. These candies have a chewy texture since there are no sugar crystals to break up the strands of amorphous sugar phase even though the presence of air bubbles provides some short character to these candies. Sugar crystals, as found in grained marshmallow and most fruit chews, also impart a shorter texture, with the short texture increasing with the amount of sugar crystals present.

The moisture content of the finished product can vary from as low as a few percent for dried marshmallow and vacuum puffed candies to as high as 25% for frappé (Table 11.1), with hardness generally increasing as water content decreases. This water content gives a water activity of between 0.4 and 0.75, meaning that many aerated candies are susceptible to drying out under normal storage conditions. Hardening over time due to moisture loss typically signals the end of shelf life for aerated confections.

11.1.1 Aerated Confections

A wide range of products fall in the category of aerated confections. Typical formulations for marshmallow, nougat, fruit chews and taffy are shown in Tables 11.2, 11.3, 11.4, and 11.5.

11.1.1.1 Marshmallow

Marshmallows come in a wide variety of shapes, sizes and textures, depending on the intended application. Marshmallows can vary in specific gravity from highly aerated products, about 0.25 specific gravity, to much denser products, with specific gravity of 0.7 or higher. Water content can vary from over 20% for fluid marshmallows to less than a few percent for dried marshmallows (often found in cereal products). Furthermore, the sugar phase of marshmallows may either be ungrained or partially grained to provide a short texture. For the most part, marshmallows are

Table 11.2 Typical formulations (in %) for deposited and extruded marshmallow

		Extruded marshmallow	Deposited marshmallow
Sucrose		30–40	30–45
Glucose syrup (62 DE)		35–45	30–45
Water		10–15	10–15
Hydrated gelatin		6–11	4.5–9.0
Gelatin (250 bloom)	33.3		
Hot water	66.7		
Flavor		0.2–0.5	0.2–0.5
Color		0.02–0.5	0.02–0.5

Table 11.3 Typical formulations (in %) for chewy and grained nougats

	Chewy nougat		Grained nougat	
Syrup phase		65–80		65–80
Sucrose	30–45		40–55	
Water	8–12		12–18	
Glucose syrup (42 DE)	43–60		32–45	
Salt	0.2–0.5		0.2–0.5	
Frappé		15–30		10–25
Protein	5–10		6–12	
Water	10–30		30–55	
Glucose syrup (42 DE)	60–80		0–10	
Sucrose	0–10		35–50	
Fat		2–5		2–5
Vanilla		0.2–0.4		0.2–0.4
Powdered sugar		–		4–6
Nuts		2–4		2–4

Table 11.4 Typical formulation (in %) for fruit chew candy

		Fruit chew
Sucrose		25–40
Glucose syrup (42 DE)		30–55
Water		6–12
Fat		6–9
Hydrated gelatin		1–3
Gelatin (250 bloom)	33.3	
Warm water	66.7	
Lecithin		0.1–0.25
Fondant		0–10
Citric acid		0.7–1.2
Flavor		0.2–0.5
Color		0.05–0.1

Table 11.5 Typical formulation (in %) for salt water taffy

	Salt water taffy
Sucrose	25–35
Glucose syrup (42 DE)	50–60
Water	8–12
Evaporated milk	0–5
Fat	2.5–5
Frappé	0–4
Mono- and diglycerides	0–0.25
Lecithin	0–0.25
Salt	0.1–0.3
Flavor	0.1–0.3
Color	0.05–0.15

stabilized with gelatin to give a gummy-like, elastic texture, although other stabilizers may be used to give different textures.

There are several different variations of marshmallow. Marshmallow is typically either extruded or deposited, and either type may be grained or ungrained. The formulation and process conditions are slightly different, depending on the desired texture and characteristics. Gelatin is the most common stabilizer used for classic marshmallows, although soy or egg proteins (or even starch) may be used, either individually or in combination with gelatin. In ungrained marshmallow, the sugar syrup must contain more than 50% glucose/corn syrup solids to inhibit formation of sugar crystals during processing or storage. Ungrained marshmallow may be formed by depositing (often in dried starch) or extruding into the desired shapes. Ungrained marshmallows may simply be dusted in starch for consumption ("jet-puffed" marshmallows), coated with sugar or enrobed with chocolate. Typical formulations for deposited and extruded marshmallows are provided in Table 11.2.

Grained marshmallow typically contains higher levels of sucrose than glucose syrup to create a supersaturated state in the sugar syrup phase of the confection. Graining is often induced through seeding with either powdered sugar or fondant prior to forming, which is usually accomplished by depositing in dried starch or extruding. A common example of a grained marshmallow is the banana-flavored circus peanut, which is deposited into dried molding starch to form the dimpled surface (mold side). Extruded, grained marshmallow may be dried to low (a few percent) moisture content, a product that is often found in breakfast cereals or hot cocoa mixes.

An ungrained form of marshmallow often used for inclusion in other foods or confections is frappé, also known at times as mazetta, egg whip or nougat créme. Frappé is often mixed into confectionery bases to make aerated products like cream centers, caramels and fudge, or nougat. In this respect, frappé is sometimes considered a sugar syrup-based carrier of air to provide aeration in other products. Frappé may be made by whipping a sugar syrup containing sucrose, glucose syrup and/or invert sugar at about 20–25% water content with a hydrated stabilizer (egg albumin is common for frappé) to low (0.25–0.35) specific gravity. The specific ingredients chosen are determined by the desired characteristics of the frappé, from light and fluffy to a more firm and robust product capable of withstanding higher agitation. Commercial frappé often contains a starch to help stabilize the aerated mass.

11.1.1.2 Nougat

The original nougat, with its origin in either France or Italy (depending on whose claim is believed), is an aerated confection made of honey, egg white and almonds. Egg protein is the main stabilizer in this type of nougat. However, nougat, like marshmallow, comes in a wide range of product characteristics, from an ungrained, extremely chewy product to grained nougat with a short texture from substantial crystallization. Nougat may be found as a distinct candy item, but in the United States is most often found in candy bars, whether grained or ungrained, and often in combination with caramel and enrobed in chocolate. Divinity or sea foam candy is basically a softer grained version of nougat.

As with marshmallow, the primary difference in grained and ungrained nougat is the relative content of sucrose and glucose syrups. Ungrained nougat must have higher levels (at least 50%) of glucose syrup solids to inhibit graining, whereas grained nougat contains more sucrose to generate a supersaturated state in the syrup phase. Graining in nougat may be promoted by seeding the cooled candy mass with powdered sugar or fondant, by agitating the candy mass at the appropriate point in the process or crystals may be allowed to form spontaneously (even during storage). Typical formulations for chewy and grained nougat are provided in Table 11.3.

11.1.1.3 Chewy Candies and Taffy

Fruit chews and taffy are typically slightly aerated, often by pulling, to give a specific gravity close to 1.0. Gelatin is often used in chewy candies, whereas the stabilizers most typically used for taffy include egg protein or starch. Chewy candies generally contain a slight level of crystalline sugar (5–10%) to provide a slightly short texture, whereas taffy generally is ungrained. The addition of a small amount (5–10%) of fat to chewy candies decreases the stickiness on processing equipment, wrappers and teeth. Tables 11.4 and 11.5 provide typical formulations for fruit chews and salt water taffy, respectively.

11.1.1.4 Vacuum-Expanded Confections

The main confection in this category is the malted milk ball, although some hard candies may also be vacuum-puffed.

In the vacuum process, small air bubbles are introduced into a cooked candy mass (4–6% moisture) through pulling or some other aeration method. After the candy is formed, often by sheeting and passing it through drop rollers to form small balls, it is placed in a type of vacuum oven. Reducing pressure while the candy is still somewhat fluid (warm, but not hot) causes expansion of the bubbles (ideal gas law) through the amorphous matrix to promote aeration (increase volume). When the puffed candy is cooled (still under vacuum), the sugar matrix solidifies into the glassy state, trapping the bubbles in their expanded state within a hardened, crunchy sugar matrix.

11.1.1.5 Aerated Hard Candy

Hard candies are often aerated to provide unique textures and colors. Aeration of hard candy is covered in detail in Section 8.3.2.2.

11.1.1.6 Aerated Chocolate

Chocolate can also be aerated, again to provide unique textures. Aeration of chocolate is covered in Section 15.6.5.

11.2 Formulations and Ingredients

The main components of aerated confections, besides air and stabilizer, are sugar and glucose syrup (Tables 11.2, 11.3, 11.4, and 11.5). Numerous other ingredients may be added to provide modified functionality, texture and/or nutritional characteristics. For example, humectants are often added to control water activity and shelf life, fats may be added to provide lubricity, emulsifiers may be added to help disperse the fat phase into a fine emulsion, and texture modifiers like starch may be added to impart specific physical properties. Colors and flavors are added to suit, as desired.

11.2.1 Air

Although the simplest (and cheapest) ingredient in aerated confections, air is also arguably one of the most important. Air should be clean, dry and free from all contaminants, including particulates, microorganisms, odors and oil droplets. When a candy is aerated by pulling (whether taffy, nougat, fruit chews, hard candy, etc.), the air in the manufacturing facility is incorporated into the mass by the continual folding and refolding. Typically, there are no concerns in regard to such aeration processes as long as good air handling facilities maintain fresh air circulation and the humidity is not too high. If humidity is above approximately 50–60%, the moisture in the air may cause problems within the candy itself and dehumidification may be necessary. If compressed air is used in pressure aeration, it must be treated to ensure that no contaminants enter the candy. Specifically, compressed air should be filtered to less than 0.3 μ prior to injection into the candy mass to remove contaminants like small oil droplets, undesired particulates and bacteria. The air should also be free from odors and any oils used in the compressors should be food grade.

Although air is the primary gas whipped into aerated confections, there are times when other gases might be used. For example, nitrogen gas might be considered for fat-based products (nougat) to minimize lipid oxidation. However, commercial use of gases other than air is rare.

11.2.2 Sweeteners

Sucrose and glucose/corn syrups are the primary sweeteners used in aerated confections, although versions of these candies can be made with other sweeteners like invert syrups and polyols. The ratio of sucrose to glucose syrup determines the likelihood and extent of graining. Higher levels of sucrose (up to 70% of sugar solids) promote graining and lead to a short texture; higher levels of syrup solids (as high as 70%) inhibit graining and give chewier candies. In some candies, such as fruit chews or grained marshmallows, fondant may be added to provide the seed for grain.

Typically, 42 DE glucose syrup is used in aerated confections, although different textures can be obtained from using other glucose syrups. Use of 63 DE glucose syrup gives a slightly softer texture, whereas high-maltose glucose syrup imparts a slightly chewier texture. Addition of a small amount of invert sugar syrup can be used to give a softer texture and to provide humectant properties by reducing water activity and inhibiting moisture loss during storage.

Sugar-free marshmallows can be made with a range of polyols. Maltitol and HSH or polyglycitol syrup (see Section 1.8.1) can be used together in exactly the same manner as sucrose and glucose syrup. Other polyols that can be used in sugar-free aerated confections include sorbitol and isomalt.

11.2.3 Stabilizers

To attain very low specific gravity in marshmallow, a stabilizer is needed. Whipping sugar syrup without a stabilizer may result in slight aeration; whereas, whipping in the presence of a stabilizer allows air to be incorporated and maintained in the candy by preventing air bubbles from coalescing during and after aeration. In many aerated confections, especially highly-aerated marshmallows, the stabilizer is a protein that orients at the air-serum interface to provide stabilization by preventing newly formed bubbles from recombining. Gelatin is by far the most common stabilizer in marshmallow, but egg albumin, dairy protein, and soy protein may also be used.

When proteins are used for aerated confections, their temperature must generally be kept below the denaturation temperature to minimize degradation. Egg, dairy and soy proteins are subject to denaturation if held at high temperatures for too long. Typically, these proteins begin to denature at about 68–70 °C (about 155–160 °F). However, denaturation is a kinetic process, meaning that the longer time it spends at temperatures above the denaturation point, the greater the extent of denaturation. Gelatin also degrades or breaks down at high temperature, with the extent of degradation proportional to time and temperature. Once the protein is denatured or degraded, it no longer provides the same level of aeration. For this reason, proteins are often added to the cooked sugar mass after it has cooled to a temperature safe from degradation. Also, since water is added with the hydrated stabilizer, the sugar syrup candy must be cooked to higher temperature accordingly to offset the addition of water back to the candy.

The choice of stabilizer is made based on the desired attributes of the final product and other factors (cost, ease of processing, religious concerns, etc.).

Each stabilizer imparts a different texture to the aerated confection. The albumens (egg, soy and dairy), typically used at levels of 1–1.5%, impart a soft, short texture. Agar (1–2%) also imparts a soft, light texture. Gum arabic (used at 20–30%), on the other hand, produces a candy with a tough, chewy texture. Alginates, used at 1.5–3%, also produce a tough texture. Modified starches may also be used in aerated confections. They produce a tough texture when used at 7–11%. Stabilizers may also be used in combinations to create unique textures and commercial blends are available for specific applications. A description of the different textural attributes of each stabilizer, along with typical usage levels, is given in Table 11.6.

Table 11.6 Stabilizers used in aerated confections

Stabilizer	Usage level (%)	Texture characteristics
Gelatin	2.0–6.0	Elastic
Egg albumin	1.0–1.5	Soft, short
Soy protein	1.0–1.5	Soft, short
Whey protein	1.0–1.5	Soft, short
Gelatinized starch	7.0–12.0	Firm, chewy
Agar	1.5	Light, soft
Gum arabic	20.0–30.0	Tough, chewy
Alginates	0.5–3.0	Tough

Data from Groves 1995

Gelatin is the most common stabilizer in marshmallows since it gives a unique elastic texture, one that can be moderated by choice of gelatin bloom strength (see Section 5.2.3.1) and the amount of gelatin used. In ungrained marshmallow, low bloom (125) gelatin used at higher levels (4–6%) gives a chewy texture, whereas high bloom (250) gelatin used at lower levels (2.5–4%) gives a shorter texture. In grained marshmallow, low bloom gelatin is used at levels of 2.5–4%.

Most stabilizers for aerated confections must be hydrated prior to use. Complete hydration is necessary to ensure that the stabilizer is fully active and the maximum results are obtained. Certain stabilizers may be very difficult to hydrate; thus, it is critical that this step be given sufficient time. Some stabilizers are prone to clumping. This can be minimized by dispersing the powders in sugars or a syrup before hydrating or dispersing with a high shear mixer. Also, an excess of water must generally be used to allow complete hydration; this water must be accounted for in the formulation for the aerated confection. Table 11.7 summarizes the minimum amount of

Table 11.7 Hydration requirements for stabilizers used in aerated confections

Stabilizer	Minimum water required	Hydration time (min)
Egg, soy, whey protein	1.0[a] (50%[b])	30
Gelatin	1.5 (60%)	30
Gum arabic	1.25 (55.6%)	45
Gelatinized starch	3.0 (25%)	–[c]
Agar	30.0 (96.8%)	–[c]
Alginates	99.0 (99%)	30

Data from Groves 1995

[a] Parts water required per 1.0 part of dry powder stabilizer

[b] % water in hydrating solution

[c] Must be fully cooked

water needed and minimum times required for hydration of different stabilizers.

11.2.4 Humectants

To moderate texture and prevent moisture loss during storage, humectants such as sorbitol, glycerol and invert sugar syrups are sometimes added to aerated confections. Addition of 1–2% humectant gives a softer product with a lower water activity that retains moisture during storage. If invert sugar syrup is used as a humectant, the total level in the candy (from addition and inversion during processing) should remain below about 4%, otherwise the candy will be excessively sticky. Addition of glycerol or sorbitol causes a significant reduction in water activity (replacement for water), which helps prevent the candy from drying out during storage while also softening the texture.

11.2.5 Fats

The addition of fats to chewy candy (nougat, chews and taffy) provides lubrication during both processing and consumption. Fats added at 3–8% of the candy mass promote easier processing (less sticking to process machinery) and lead to less stickiness on the teeth during consumption. However, fats have a negative effect on aeration since they migrate towards the air interface and cause breakdown of air bubbles. Thus, their addition must be carefully controlled, particularly in nougat, to ensure that aeration is not inhibited or lost.

Typically, fats are not added in marshmallow formulations since fats tend to depress whipping ability. Marshmallow is intended to have a low density and high air content, which precludes the addition of fat. In nougats, less aeration is desired and the highly viscous continuous sugar phase tends to hold air bubbles, so some fat can be accommodated in the formulation, particularly if added late in the process, without losing texture characteristics. Liquefied fat is often blended into the warm aerated mass, with as little shearing as possible, as one of the final process steps prior to forming. When the nougat is cooled, the fat globules become semi-crystalline and provide the desired lubricity without affecting aeration. In chews and taffies, the extent of aeration is sufficiently low that the negative effect of fat is not a problem and the fat can be added at the beginning. This is particularly true for candy that is pulled since the high viscosity of the candy matrix on the pulling machine (or hook, if pulling is by hand) stabilizes the air cells incorporated by folding and re-folding.

Typically, the fats used in chewy candies are modified vegetable fats, chosen primarily for their low price, melting properties, and resistance to oxidation. Fats typically add little in the way of flavor to these products; however, their physical attributes are important to finished product characteristics. They should be semi-solid at room temperature to provide stand-up properties and prevent oiling off, with a melting temperature less than mouth temperature so there is no waxy mouthfeel. A melt point of 33–35 °C (91–95 °F) is generally considered best for fats used in taffy, although higher melting points, 35–40 °C (95–105 °F), may be more appropriate in warmer environments.

Since the fats are exposed to air within the candy itself, lipid oxidation (see Section 4.2.3) is a problem that can result in rancid off-flavors. Often, nonlauric fats (palm, soy, cottonseed, etc.) modified to have the appropriate melting properties are used since lauric fats (e.g., coconut, palm kernel) oxidize readily to produce soapy off-flavors. Palm fats (or certain of its modifications) may be used to minimize *trans* fat content.

11.2.6 Emulsifiers

The addition of fats to aerated chewy candies (nougat and taffy) generally dictates that an emulsifier be added to help disperse and stabilize the fat globules during processing (see Section 4.6), particularly when the candy mass is still fluid. However, the viscosity of the continuous sweetener phase generally prevents fat globules from coalescing and prevents oil separation; thus, emulsifiers are not necessarily needed to stabilize the emulsion.

When used, lecithin is the most common emulsifier found in aerated confections, although glycerol monstearate (GMS) and sugar esters can also be used. GMS in particular helps to reduce stickiness of nougats and chewy candies. Levels of emulsifier use are generally low, between 0.1% and 0.2%.

11.2.7 Texture Modifiers

Low levels of texture modifiers may be used to influence physical properties and eating characteristics, particularly in chewy candies (nougat and taffy). Starch, dextrin, gums, pectin, and gelatin may be added to provide specific textural effects. The use of starch in taffy, for example, helps improve stand-up properties (reduces cold flow) and imparts a slightly shorter texture to the candy piece. In some cases, a portion of the starch used in taffy may be added after the cook (but before pulling). The presence of intact starch granules helps prevent cold flow and provides a shorter texture. High molecular weight saccharides, like dextrins, also enhance chewing characteristics in fruit chews and taffy.

The addition of fondant or powdered sugar to aerated candies is a form of texture modification in that the crystals provide a shorter texture to the candy. The extent of short texture characteristic depends for the most part on how much of the sugar is in crystalline form (also a function of water content and sucrose to glucose syrup ratio). Highly grained candies (as in some marshmallows) can have an almost crumbly texture, grained nougats with intermediate crystal content have a short and soft texture, and lightly grained candies (like fruit chews) are somewhat short but still retain a significant chewy and elastic texture.

11.2.8 Fruit Juice

To appeal to a more health-minded consumer, many fruit chews are now formulated with fruit juice and/or concentrate. Since fruit juice concentrates typically contain high glucose content, the other sweeteners must be chosen carefully to provide a balanced saccharide profile lest the candy be excessively soft and sticky. Another consideration with fruit juices added prior to cooking is that they lose a substantial amount of flavor through volatilization at boiling temperatures and thus, other flavorings are still typically required. Some juices (for example, black carrot juice concentrate) may also be considered colorants.

11.2.9 Organic Acids

It is common to add organic acids to complement fruit-flavored chewy candies (fruit chews and taffy). As in other candies, acids added at a low level, less than 1%, bring out the fruit flavors. In some chews, higher levels (1–2%) of organic acids, including citric, malic, tartaric, fumaric or ascorbic acid, may be added, for example, to provide a sour experience. Often the best flavor pairings happen when the organic acid matches the base flavor. For example, lactic acid matches with dairy flavors, citric acid with citrus flavors, and malic acid with strawberry flavors.

11.2.10 Flavors

Water, glycol and alcohol-based flavors are best suited for aerated confections. Oil based flavors should not be used for highly aerated products like marshmallow since they might cause a loss in aeration. For this same reason, low fat cocoa powder should be used instead of chocolate liquor because of its lower fat content.

Flavors should be stable when aerated and verified that they do not react with the whipping proteins to cause denaturation. Flavor usage is greatly dependent upon the strength of the flavor and customer expectations. Flavor usage is often in the 0.2–0.5% range.

11.2.11 Colors

As with flavorings, it is prudent not to use oil-based dyes in highly aerated confections, although they may be acceptable in low aeration confections such as pulled taffies. Consistency in color is easier with a predispersed dye than with a dye powder, which can cause speckling. Usage levels (especially for dark color shade) tend to be higher than in other confections since aeration imparts whiteness.

11.2.12 Gelation Aids

In some types of marshmallows such as sugar free or standard marshmallows where quick setting of the gelatin is required for the production process, a gelation aid may be added to the formulation. Sodium hexametaphosphate and metal salts such as calcium chloride help promote rapid gelation by forming an ionic bridge between gelatin strands. Rapid setting of gelatin is needed for extruded marshmallow since the marshmallow rope would flatten out as it leaves the extruder and is transferred to the conveyor belt.

11.2.13 Active Ingredients

Lightly aerated chewy candies are good carriers of active ingredients and various health-promoting products can be found on the market. For example, a chewy nougat product contains calcium carbonate to promote bone strength in certain individuals. Other types of active compounds that might be found in such candies include vitamins, caffeine, proteins, essential oils, and other extracts (e.g., lutein).

11.2.14 Inclusions

Of the aerated candies in this category, nougat is the one most likely to contain inclusions. In nougat, it is common to find nuts and fruit pieces; in fact, the original nougat from France and Italy contained nuts and perhaps fruit as well. The inclusions are typically chopped into fine pieces and blended into the candy mass just prior to cooling, solidification and forming. Inclusions increase the overall specific gravity of the piece, although the nougat phase remains highly aerated, and provide a unique contrast between the dense solid inclusion and the lighter, more aerated nougat.

11.3 Processing

Manufacture of all aerated candies, except those that are vacuum expanded, generally follows the process shown schematically in Figure 11.1. Differences in method of cooking and aeration are based on the nature of the product. After the sweeteners have been mixed together, the sugar syrup is cooked to the proper temperature to give the desired moisture content in the finished product. The stabilizing agent may be added either before cooking or after, depending on the process. The batch is then cooled and aerated to produce a candy with reduced density. The method and order of ingredient addition, the aeration step, and forming processes are steps that depend to some extent on the type of aerated products.

11.3.1 Dissolving and Cooking

As with most candies, the sweeteners are mixed together and heated to dissolve any crystalline materials. The syrup mixture is then cooked to the specified temperature to obtain a candy mass with the desired moisture level. Typical cooking temperatures are in the range of 107–110 °C (225–230 °F) for marshmallow, 123–129 °C (253–264 °F) for nougat, and 121–132 °C (250–270 °F) for fruit chews and taffy. It is important to control the cook temperature in order to control

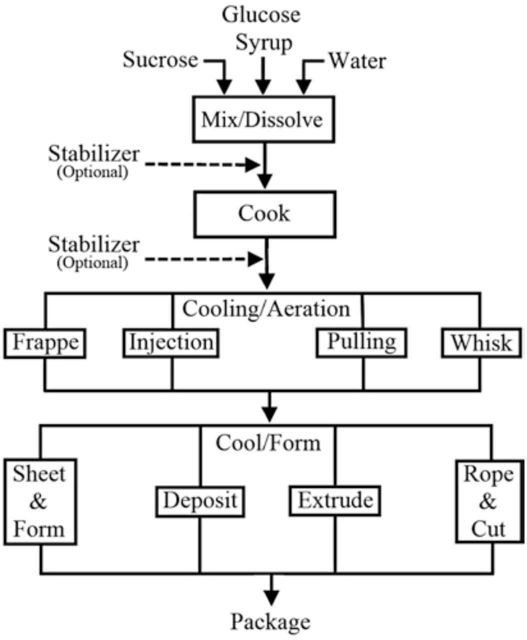

Figure 11.1 Schematic of typical process for manufacture of aerated confections

moisture content. Especially in nougat, chews and taffy, slight differences in moisture content may be sufficient to cause a product to exhibit cold flow (moisture too high) or be too hard (moisture too low). Thus, control of cooking temperature is critical to obtain uniformly consistent product with the desired textural and sensory properties.

Variance in texture can also occur when changes in cooking time are found. Increased cooking times in batch cooking systems can promote sugar inversion, which results in a softer texture and increase stickiness. Water quality should be monitored for pH and mineral content since this can also have an effect on sugar inversion. Changes in barometric pressure and relative humidity may also have an effect on the final product texture.

The simplest cookers are batch kettles, heated with either a steam jacket, electric heating element or open flame. These may require manual stirring or have internal stirrers, usually blades that sweep the surface. Large scale, continuous cookers (i.e., micro-film cookers, shell and tube heat exchangers, plate heat exchangers, scraped surface heat exchangers, etc.) may be used for higher throughputs and fully automated production lines.

11.3.2 Stabilizer Addition

Before a stabilizer can be used it must be properly hydrated so that all of the benefits of the proteins can be realized. Hydration is dependant upon the ratio of water to stabilizer (see Table 11.7 for minimum moisture and time required) and the time allowed for hydration. Typical hydration for gelatins and albumens is 2:1–4:1 water/stabilizer for 30 min. Exact hydration time is dependant on ratio and granulation size. It is also best practice to use cold water for proper dispersion and to prevent formation of ‘fish eyes’.

In marshmallows, hydrated gelatin may be added either before or after cooking. Although adding gelatin after the cooked syrup has cooled is preferred, it is not uncommon in batch cooking that the hydrated gelatin is added to the batch directly at the end of the cook, along with other heat sensitive ingredients (e.g., flavors). In larger continuous systems, gelatin and other proteins may be metered into the cooked syrup through an injection port ahead of an in-line static mixer.

When hydrated stabilizer is added after cooking, the initial cook temperature of the sweetener syrup must be set a little higher than what would be expected for the water content of the finished product to offset the amount of water added back. That is, the sugar syrup is cooked to slightly higher temperature to have reduced water content, which is then brought up to the desired moisture level by addition of the aqueous hydrocolloid.

To simplify the process, gelatin (and sometimes other proteins) may be added directly to the sugar syrup (slurry) and the entire mass cooked quickly to the desired temperature. Since protein degradation occurs at temperatures above about 68–70 °C (about 155–160 °F), cooking the protein with the sugar syrup means that some degradation will occur. This can have a negative effect on the aeration properties and the characteristics of the final product. However, if cooking time is short, the amount of degradation that occurs may be sufficiently small that the loss of aeration and structure is offset by the advantages of a single cooking step, without the need for secondary addition of hydrated stabilizer.

According to kinetic reaction laws, the rate of degradation increases exponentially as temperature increases and the extent of degradation is related to the length of time at elevated temperature. For example, it takes about 30 min at 95 °C (203 °F) for gelatin to lose about 10% of its bloom strength (pH 5), whereas at 80 °C, only 2–3% loss in bloom strength is observed in 30 min and at 60 °C, there is only about 1% change in bloom strength over that time. Lowering pH results in significantly faster degradation rates, with between 5% and 10% degradation in 30 min at 60 °C and pH 2. In modern rapid continuous cooking technologies, gelatin may experience temperatures over 120 °C (249 °F), but only for a short time (less than a minute). Although some gelatin degradation will occur at these conditions, which could potentially lead to less aeration capacity and weaker gel strength, the extent of degradation may be small enough that a manufacturer may choose to cook the gelatin directly in the sugar syrup. Egg proteins denature more quickly than gelatin and are most often added to the syrup after the cook.

Another negative consequence of cooking the protein with the sugar syrup is browning and discoloration. As one of the main reactants in the Maillard browning reaction (see Section 1.4.3.1), protein (egg, soy, whey and gelatin) reacts with reducing sugars to produce brown pigments and caramel flavors when heated. Continuous cooking technologies with short residence times at high temperature minimize color formation so that browning generally is not a problem.

11.3.3 Cooling

In general, the candy mass for aerated confections must be cooled somewhat before aeration, especially if the stabilizer is added after cooking. If not cooled sufficiently, the stabilizing agent may denature or degrade and no longer function properly as a whipping agent. On the other hand, if the candy mass is too cold before protein is added, it will be difficult to get a homogeneous dispersion into the sugar syrup. It is preferred to add gelatin and other protein sources once the syrup has cooled to 77 °C (170 °F) to reduce danger of severe degradation, although lower temperatures, around 65.5 °C (150 °F), are preferred to minimize negative effects. As noted above, however, the extent of degradation depends on both temperature and time, so in general, the higher the addition temperature, the shorter the time before extensive degradation.

For marshmallow, it is important that the candy mass be cooled to just above the setting point of the gelatin before whipping. It is, in part, gelation of the gelatin that keeps air bubbles separate during cooling and promotes aeration during whipping. If the candy mass is too warm during whipping, the air bubbles will coalesce and specific gravity will not be sufficiently low. Typically, the candy mass is cooled to 45–55 °C, just above gelatin's melting point, (113–131 °F) prior to aeration.

Cooling of the candy mass prior to stabilizer addition and subsequent aeration may be accomplished in several ways. In small-scale operations, the candy mass from a batch cooker is simply poured onto a cold table for cooling, with acids, flavors and other heat sensitive ingredients being added prior to folding. The cooling drum is another common method of cooling candy mass for nougat, chews and taffy. Cool water circulating inside the drum provides rapid cooling of a thin layer of sugar syrup. Drum rotation is sufficiently slow that the candy mass is cooled to the desired temperature after one-half to two-thirds of a rotation of the drum. The cooled candy mass is scraped off the drum and collected for further processing. In larger continuous operations, cooling of marshmallow and nougat candy mass may be accomplished in a scraped-surface heat exchanger (e.g., Votator). Other types of heat exchangers (plate, shell and tube, etc.) are typically not sufficient for cooling such thick candy masses.

11.3.4 Aeration

The extent and method of aeration depends on the type of candy being made. Numerous options are available although highly aerated products like marshmallow generally require different equipment than lightly aerated products like taffy. Aeration may either occur from simple open air whipping to more precise air injection during extrusion.

11.3.4.1 Marshmallow and Nougat

In marshmallow, aeration takes place at warm temperatures, when the candy mass is still liquid above the melting point of gelatin. One of the simplest methods for aeration of marshmallow is whipping in a kettle or bowl with a whisk-type mixer, often called a planetary mixer. The whisk action introduces air into the candy mass through a constant folding and refolding process. Larger air pockets are then broken down into smaller air bubbles by the continued shearing action of the whisk. The whisk itself wipes off the surface of the bowl to prevent build up on any one spot. The candy mass is whipped until it reaches the desired density, as measured by periodically weighing the candy in a cup of known volume. Densities as low as 0.3 or 0.4 can easily be achieved with a planetary mixer operated under the right conditions. However, besides being a batch process, there are several disadvantages to the planetary mixer method. For example, up to 2–3% water loss may occur during beating, which must be accommodated in the initial formulation. Also, since it is a batch process, control of aeration is less precise than with some other aeration methods, giving a wider variation in specific gravity of the finished product.

For better control, and more rapid aeration, a pressure mixer may be used. Enclosed kettles, or pressure whisks, are operated with (filtered) compressed air injected under pressures of up to 345 kPa (50 psig). Specific gravity is controlled by the amount of air injected into the mass, with densities as low as 0.3 being easily attained in marshmallow production. The whipping process is essentially identical to that described in the previous paragraph.

For large-scale production, aeration of marshmallows may be done in continuous pressure beaters, a process that also accomplishes several other steps (cooling and forming) at the same time. The cooked sugar syrup containing the hydrated gelatin is fed into the mixer, where a controlled flow of air is injected under pressure. A cooling jacket provides temperature control as the candy mass is whipped. The mixing head typically contains a rotor/stator arrangement to provide shearing action so that the relatively large air bubbles injected into the mixer get broken down into very small bubbles by the high shear forces (see Section 11.4.1.1.2). A back-pressure valve at the outlet of the mixer allows pressure to be maintained in the mixer. The tiny bubbles in the candy mass within the mixer expand slightly according to the ideal gas law as the candy passes through the outlet orifice. Continuous pressure beaters can also be used to aerate nougat. Because of the higher viscosity with these products, higher pressures are required to force aeration.

The size of air bubbles produced in marshmallow from a continuous pressure beater is determined by numerous factors, including (1) the applied shearing forces, which are a function of syrup viscosity (temperature and composition), the rotor/stator design (pins, head size), and rotational speed, (2) whipping temperature, (3) residence time within the mixing head, which is governed by the syrup pump rate and air injection rate, and (4) the pressure in the mixing head. Increased shearing force generally leads to smaller air bubbles; however, if too much heat is added to the marshmallow through mechanical energy input and frictional heat released, the decreased local viscosity can lead to coalescence and ultimately, larger air bubbles. Thus, temperature control is important in continuous aerators. A stiff marshmallow product with density of 0.5–0.7 g/mL exits through the outlet die where it is either cut in the appropriate sized pieces or collected on a take-away conveyor operating at the same speed as the product exits the extruder. Outlet temperature is critical since the gelatin should be starting to set up as it exits the aerator so that it does not collapse on the conveyor. Gelation aids, like sodium hexametaphosphate, can be added to the formulation to help solidify the marshmallow more quickly.

In some operations (nougat in particular), the frappé method is used to aerate the candy mass. In this case, frappé is made by separately whipping a portion of the sugar syrup at cool temperatures. Any of the aeration technologies noted above may be used to make the frappé, typically with a very low specific gravity (0.2–0.3). The bulk of the sugar syrup is cooked to the desired water content (accounting again for the water being added back in the frappé), cooled, and mixed with the frappé. The ratio of frappé added to the cooked sugar syrup and the specific gravity of the frappé govern the specific gravity of the finished candy.

11.3.4.2 Chews and Taffy

It is not unusual to see taffy being pulled by hand at fairs and resort areas. After cooking and cooling to the appropriate temperature, a plastic candy mass is placed on the hook and pulled downwards with half on either side of the hook. The two pulled ends of candy are brought together and looped back up over the hook. The two new ends are pulled down again and the process is repeated until the candy has been aerated to the appropriate level. Air is incorporated into the candy as it is stretched and folded over itself. Unlike other whipping methods, pulling creates nonspherical air pockets due to the stretching and refolding of the candy. A change in color is also observed as the candy is pulled, with color becoming lighter, almost pastel-like. Typically only light to moderate levels of aeration (density of 0.9 g/mL) can be accomplished with the hook. However, hand pulling is no longer used in commercial operations, having been replaced by more convenient and controlled pulling devices or automated whipping technologies.

Pulling machines, either horizontal or vertical, provide automated aeration of candy batches. They are used still for hard candy (see Section 8.3.2.2), chewy candies and taffy, among other applications. The plastic candy mass is mounted on the hooks and the machine pulls the mass until the desired aeration level has been reached. Moderate aeration levels (0.8–0.9 g/mL) can be achieved with pulling machines.

11.3.5 Final Ingredient Addition

After aeration and just before the final cooling and forming steps is often when other ingredients, such as fats and inclusions (and sometimes colors and flavors) are added, particularly for nougats. At this point, the candy mass has numerous small bubbles from the aeration step and these bubbles are stabilized to some extent by the stabilizer. However, the bubbles at this point are still prone to coalescence, where smaller bubbles combine to form larger bubbles with less surface area. Coalescence is promoted by the fluidity of the candy mass and by mixing, as this brings the bubbles together and promotes breaking of the interface between bubbles. Although mixing must be kept to a minimum at this point, sufficient mixing is needed to completely incorporate fats, colors and flavors into a homogenous candy mass at this point. Liquid fat can also destroy aeration so mixing in the fats should be as gentle as possible to retain the desired aeration.

11.3.6 Cooling and Forming

Once the final ingredients have been incorporated, the candy mass is cooled and formed into the desired shapes (or formed and cooled, depending on the technology). Numerous forming methods are available, with the choice depending on the nature of the candy being formed.

Marshmallows are typically formed either by depositing or by extrusion. Fluid marshmallow formulations are deposited into depressions in starch trays and solidified by allowing the trays to stay overnight in a warm, dry room to promote drying to the final moisture content (see Section 12.3.1.2.2.1 for more description of the starch mogul process). Products with well-defined shapes, like seasonal candies (Santas, turkeys, etc.) or promotional items that will be enrobed in chocolate, are often made this way. The fluid nature of the deposited marshmallow allows the candy to fill in details of the starch mold. Alternatively, marshmallow can be deposited directly onto a moving conveyor. In this case, the marshmallow must be formulated to the final moisture content and the gelatin must set quickly after depositing in order to retain the desired shape. Interesting candy designs (including chick shapes, with a beak) can be created by coordinating the motion of the depositing heads with the conveyor. Center-filled marshmallows (chocolate paste, fruit filling, etc.) can be formed by co-depositing a center around the marshmallow exterior. After depositing on a conveyor, the marshmallows are dusted with starch or sugar particles to prevent sticking.

Marshmallows can also be formed by extruding the candy mass through an orifice into the desired shape. Extruded marshmallows can be cylindrical in shape, with pieces cut in short lengths (e.g., jet-puffed marshmallows), or they can take almost any desired shape (stars, etc.) depending on the nature of the orifice through which the candy is forced. Co-extrusion technology can be used to create multi-colored marshmallow ropes or twists, or to put designs within the marshmallow rope. To prevent sticking of the final product, extruded marshmallows are typically coated with a dried starch powder, with the excess starch removed by tumbling the candies in a rotating screen drum.

Nougat, fruit chews and taffy, with higher density, are often formed using standard methods of either slabbing and cutting or forming into ropes in a batch roller (similar to that used in hard candy forming; see Section 8.3.1.5). Here, the plastic candy mass may be formed into ropes on the batch rollers and sized to the desired diameter prior to being cut and wrapped. Fruit chews and taffy are commonly formed in this way. Multi-colored and design (e.g., pumpkin face) taffy is made by blocking strips of different colors of taffy into a log for pulling on the batch rollers, in the same fashion as cut rock (see Section 8.3.2.1).

For a nougat that will form the base of a candy bar (e.g., enrobed in chocolate), there are many options from very manual to very automated. A typical automated line cools the cooked nougat to the desired temperature on a cooling wheel, which is then formed to the proper slab thickness by passing through sizing rollers. The slab is further cooled in a tunnel before being cut into strips with rotating slitter knives. The separated ropes of nougat are then guillotined to the proper length before being enrobed in chocolate.

11.4 Product Characteristics

The primary component that distinguishes aerated candies from other confections is air. The amount of air incorporated and nature of the bubble size distribution, along with the hydrocolloid used to stabilize the air, have considerable impact on product qualities such as texture, flavor release, and shelf life.

11.4.1 Microstructure

Arguably the most important structural aspects of aerated candies are the numerous small bubbles (or air cells) distributed throughout a continuous aqueous sugar phase. The stabilizer acts at the air/sugar interface to help stabilize the air bubbles (Figure 11.2). The continuous sugar phase may sometimes be amorphous (ungrained) and sometimes partially crystalline (grained). In grained confections, many small sugar crystals are distributed throughout the continuous aqueous sugar phase (Figure 11.3). The amount of air incorporated, their bubble size distribution, the viscosity of the continuous sugar phase, the elastic characteristics of the stabilizer, and the presence of sugar crystals are important parameters that affect the textural properties of aerated confections. In those candies that contain fat, the dispersion of fat globules, generally being partially crystalline, intermixed with the air bubble dispersion can also have considerable effect on the physical properties.

11.4.1.1 Aeration

The process of aeration generally involves two steps. First, air cells must be introduced in some process and second, those air cells must be stabilized to prevent them from coming back together. In many cases, intense shearing action within the aeration/mixing device helps reduce air bubble size.

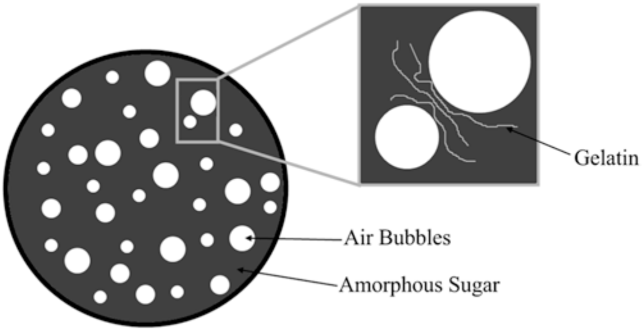

Figure 11.2 Schematic representation of ungrained marshmallow structure

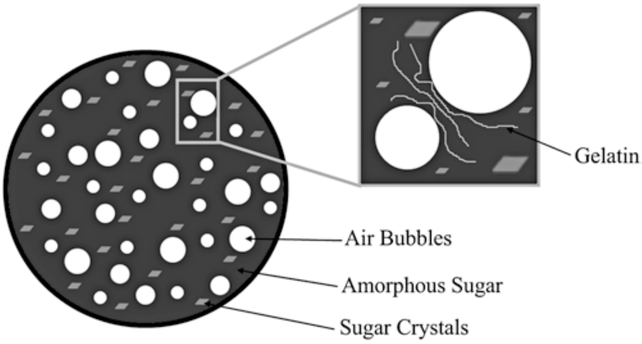

Figure 11.3 Schematic representation of grained marshmallow structure

11.4.1.1.1 Air Cells in Confections

Aeration can be accomplished by whipping a fluid candy mass open to the air, by direct injection of air into the liquid mass in an enclosed vessel, by pulling a plastic candy mass or by chemical aeration, with the nature of the air cells being quite different between the processes (see Section 8.3.2.2 for more details on aeration mechanisms). Whipping of a fluid mass, where the shear forces continually break down air bubbles into smaller and smaller sizes, typically results in formation of numerous small spherical bubbles. Pulling a plastic candy mass simply folds air pockets into the plastic candy mass, giving irregularly-shaped, smeared air cells. Chemical aeration produces air pockets dependent on the chemical reaction rate within the candy mass. Figure 11.4, a scanning electron micrograph of a jet puffed marshmallow aerated in a continuous air injection process (Zeigler and Decker 2002), shows the generally spherical nature of the air bubbles formed during whipping of a fluid mass. Compare the air cells found in a pulled taffy product (Figure 11.5), where irregularly-shaped air pockets are introduced by continually pulling, stretching and refolding the plastic candy mass. Finally, Figure 11.6 shows the smooth rounded bubbles formed from chemical aeration, in this case in an after dinner or grained mint.

The average bubble size in a typical marshmallow is between 20 and 25 μm, although bubble size may vary from as small as about 10 μm to well over 40 μm. Typically, in marshmallow, the largest number of smallest sized bubbles is desired to give the smoothest texture. In batch whipping, it is possible to take samples periodically for microscope analysis. With this method, the reduction in bubble size during whipping can be followed. The point at which bubble size begins to increase again is the point of overwhipping, where additional agitation simply serves to promote bubble coalescence rather than break down. Unfortunately, methods to study air cell formation in other aeration technologies are quite limited.

Air bubbles in finished products have been viewed in a variety of ways. Optical microscopy,

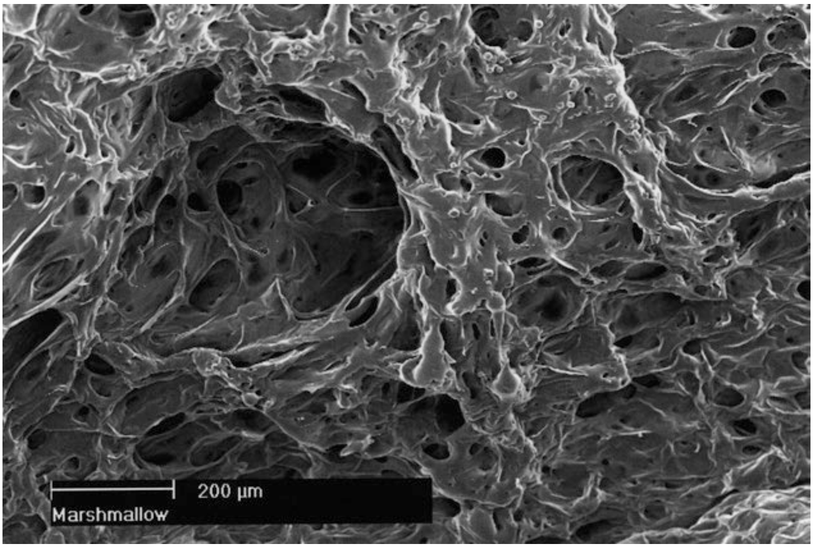

Figure 11.4 Scanning electron micrograph of jet-puffed marshmallow made by aeration in a continuous air injection process (From Ziegler and Decker (2002), with permission)

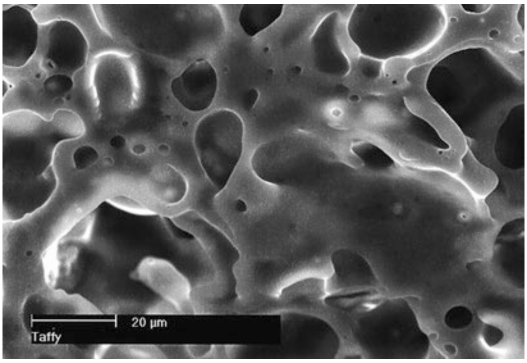

Figure 11.5 Scanning electron micrograph of taffy aerated by pulling (From Ziegler and Decker (2002), with permission)

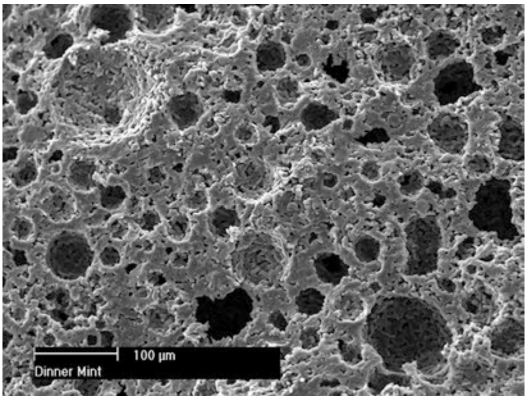

Figure 11.6 Scanning electron micrograph of grained after dinner mint aerated by chemical aeration (From Ziegler and Decker (2002), with permission)

particularly reflection stereomicroscopy, may be used in certain circumstances to visualize air bubbles. Groves (1995) suggests placing a sample of marshmallow between a slide and cover slip (without smearing) on an optical microscope to follow the development of air bubbles during batch whipping. The most commonly used method, however, for characterizing air cells in aerated products is scanning electron microscopy (SEM). Typically, sample preparation involves rapid cooling to solidify the candy matrix, followed by freeze fracturing and dehydration to produce a surface suitable for exposure to an electron beam for visualization. Decker and Ziegler (2002) discuss the difficulties associated with SEM sample preparation for aerated confections, but present a variety of informative images of aerated confections using this technique. Decker and Ziegler (2002) also discuss the possible use of X-ray computed tomography (CT) for imaging aerated confections but note that resolution is the main limitation of this new technique (see Lim and Barigou 2004, for more about X-ray CT). Reinke et al. (2016) used synchrotron

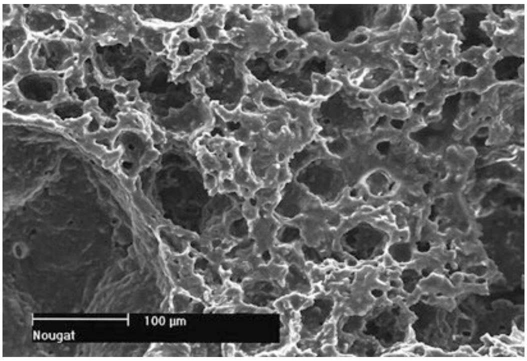

Figure 11.7 Scanning electron microscope image of grained nougat showing two distributions of air cells (From Ziegler and Decker (2002), with permission)

x-ray tomography to investigate the aerated structure of chocolate.

As noted earlier, the nature of the air cell distribution in an aerated confection depends on the process by which it was aerated. For example, Figure 11.7 shows the air bubble distribution in a grained nougat made by the frappé method. In this case, the numerous small air bubbles of about 20–40 µm were produced from addition of the frappé. A second population of larger (greater than 100 µm) air bubbles was also observed (see lower left corner of Figure 11.7). These larger bubbles were introduced when the cooked sugar syrup was added to the frappé to create the nougat.

11.4.1.1.2 Continuous Aeration: Technology and Mechanisms

Modern continuous aeration methods generally use rotor and stator technology to inject air and create small air bubbles. A photo of a continuous marshmallow aerator is shown in Figure 11.8. As the rotor spins, the sugar syrup and injected air bubbles are sheared between the stationary stator pins and pins on the rotor. High rotor RPMs and narrow clearances between rotor and stator cause high turbulent shear stresses on the candy mixture, resulting in substantial break-down of air bubbles. The shear forces are dependent not only on rotor RPM, but also on the number of pins and the surface area of the rotor pins.

In principle, the reduction in air bubble size in a rotor-stator device can be explained through the Weber number, We, given as (Hanselmann and Windhab 1999)

$$We = \tau d / 4\sigma \tag{11.1}$$

Here, τ is the shear stress applied between rotor and stator, d is bubble size, and σ is the interfacial tension between the air bubble and the sugar syrup. Typically, for turbulent flow, a critical Weber number, We_c, is defined, which correlates the shear forces with the air bubble size. The maximum bubble size, d_{max}, then can be written as

$$d_{\max} = 4\sigma We_c / \tau \tag{11.2}$$

From Eq. 11.2, several effects can be seen. First, air bubble size is inversely proportional to shear stresses applied in the mixing head. Higher shear stresses, as noted above, result in proportionately smaller bubble size. Second, the interfacial tension has a direct effect on maximum bubble size. Lower interfacial tension results in smaller air bubbles.

Once an air bubble has been reduced in size by shearing, however, it must be stabilized in some way to prevent coalescence and phase separation. Stabilization occurs by preventing the bubbles from coming back together, either through high viscosity of the continuous phase and/or through addition of a stabilizing agent that adheres to the bubble surface and thereby prevents coalescence. Both mechanisms are important in aerated confections, with viscosity playing a major role in chewy and taffy candies, and protein surface stabilization being more important in marshmallow products. Ultimately, the stabilization of air bubbles in all aerated confections occurs by a combination of the two mechanisms, viscosity and surface coating. In some cases, solid particles like sugar or fat crystals may also influence air bubble stability. Furthermore, the presence of liquid fat at an air bubble interface leads to rapid coalescence.

If not stabilized appropriately, the finely divided air bubbles in aerated confections can come back together and lose their individual character, increasing the average size. Mechanisms of bubble re-formation are coalescence, drainage and disproportionation. Coalescence is the action

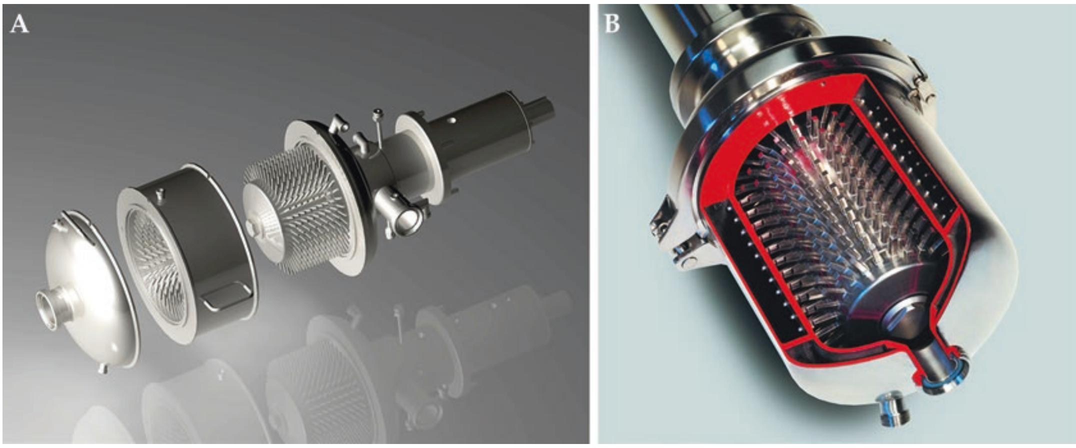

Figure 11.8 Continuous marshmallow aerator of rotor-stator design: (**a**) Entire assembly; (**b**) rotor-stator head (Courtesy of Haas-Mondomix)

of two distinct bubbles joining together to form a single larger bubble. The two bubbles must be in close proximity and not have any components preventing them from coming together. Surface-active agents, like fats and emulsifiers, can reduce the interfacial tension at the bubble surface and promote coalescence. Drainage refers to the flow of the liquid phase around the bubbles, which causes bubbles to come into closer proximity and leads to coalescence. Higher viscosity and lower temperature inhibit drainage and help to stabilize air bubbles against coalescence. In some cases, disproportionation can occur, where small bubbles shrink and large bubbles grow due to the thermodynamic difference in stability of bubbles of different sizes. In most confectionery applications, disproportionation is generally not a problem. However, in many aerated confections, there is some degree of air cell coalescence (or partial coalescence) during storage with an interconnected air cell network formed (to varying degrees) over long-term storage.

11.4.1.1.3 Graining

As shown schematically in Figure 11.3, grained marshmallow, grained nougat and most chewy candies contain small sugar crystals dispersed throughout the continuous aqueous sugar phase. In some respects, this dispersion of crystals is quite similar to that found in fondants and creams, except there is much higher crystal content in fondant. Whereas fondant typically has 50–60% crystalline content, grained marshmallow and nougat have only about 20–30% and fruit chews have less than 10%. A polarized light microscope image of the crystalline structure of grained nougat (from a commercial candy bar) is shown in Figure 11.9. Individual crystals smaller than approximately 20–30 μm are seen. These are dispersed throughout the continuous phase and induce a short texture to the nougat. Figures 11.10 and 11.11 show electron micrographs of grained nougat and marshmallow, respectively. Although it is sometimes difficult to identify individual sugar crystals with this technique, the entire structure of the grained candies is clearly different from that of ungrained candies (compare Figures 11.4 and 11.5 for marshmallow and nougat, respectively). Even though it may not be perfectly clear from these images, sugar crystals also have an impact on air cell formation and stabilization, through a combination of their surface-active behavior and their effect on the viscosity of the continuous sugar phase.

The extent of crystalline content present in aerated candies is primarily a function of (1) the relative amount of crystallizing species (sucrose) to inhibitors (glucose syrup) present in the formulation and (2) the water content. Although sucrose is usually the main crystallizing component in aerated confections, sugar-free versions would contain sugar alcohol (sorbitol, isomalt, maltitol, lactitol, etc.) crystals and some doctoring component (e.g., maltitol syrup, etc.) to

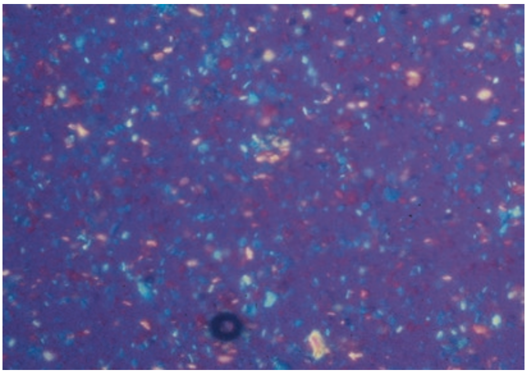

Figure 11.9 Polarized light microscope image of sugar crystals in the grained nougat of a candy bar (magnification 40×)

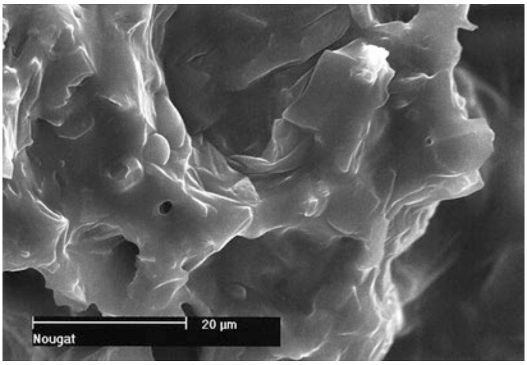

Figure 11.10 High magnification scanning electron microscope image of grained nougat (From Ziegler and Decker (2002), with permission)

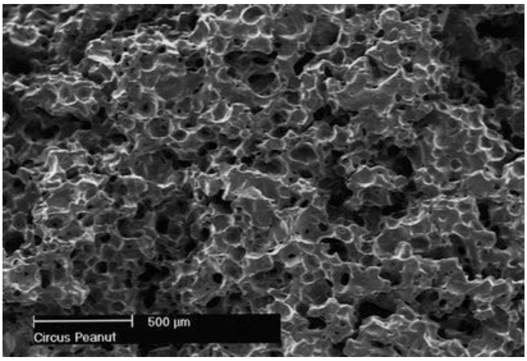

Figure 11.11 Scanning electron microscope images of grained marshmallow – circus peanuts (From Ziegler and Decker (2002), with permission)

moderate the extent of graining. The state diagram approach discussed in general in Section 2.10, and specifically for fondant in Section 9.4.1, could be applied to aerated confections to determine the crystalline content of the sugar phase. Ergun and Hartel (2009) used the phase/state diagram approach to compare grained and ungrained nougats. Based on estimates of sucrose solubility in the presence of glucose syrup in the two formulations, it was found that the liquid phases of both grained and ungrained nougats were supersaturated. The grained nougat, however, was seeded with powdered sugar to set the grain, whereas the ungrained nougat had sufficient glucose syrup present to inhibit graining even over long periods of time.

Empirically, candy makers know that if there is more sucrose than other sugars (glucose syrup, invert sugar, etc.) in a formulation, the likelihood of graining is high. The higher the ratio of sucrose to other sugars, the greater the likelihood of crystallization, the faster it will take place and the more crystalline material will form. Therefore, aerated candies that are designed to grain should be formulated with higher ratios of sucrose to glucose syrup. Ungrained aerated confections should have less sucrose, with either glucose syrup, invert sugar or some other sugar added in its place to prevent crystallization. Replacing sucrose with other sugars is effective in preventing crystallization in two ways. First, there is less sucrose present so the residual supersaturation will be significantly less than for grained confections and second, the other sugars act as inhibitors that reduce the rate of crystallization. If there are sufficient quantities of other sugars present, sucrose graining does not occur over the life time of the product despite the residual supersaturation.

An empirical approach to understanding and controlling crystallization in nougat relates the ratio of crystallization accelerator sugars to that of crystallization inhibitors (Ergun and Hartel 2009). In this approach, the Graining Factor (GF) is defined as:

$$\mathrm{GF}(\%) = \frac{[\text{accelerator sugars}]}{[\text{accelerator sugars} + \text{inhibitor sugars}]} * (100) \qquad (11.3)$$

For example, in a nougat containing only sucrose and glucose syrup (and discounting stabilizer and fat as inhibitors), GF would be calculated as the ratio of the total sucrose content to the sum of total sucrose plus glucose syrup contents (on a dry basis). If there were equal parts of sucrose and glucose syrup on a dry solids basis, GF would be 50%. Based on empirical evidence (Y. Noda, personal communication), a formulation with GF less than about 45% would be unlikely to support sucrose crystals, whereas formulations with higher GF could potentially be grained. Formulations with increased GF would be expected to have increased crystal content.

Comparing the empirical GF approach to the fundamental phase diagram approach (Section 9.4.1), one can see that GF represents only one aspect of the phase diagram. The critical GF (above which crystalline sugar might be expected) correlates to the equilibrium condition; however, the ratio of sucrose to other sugars by itself is not sufficient to identify that equilibrium exactly. Water content, temperature and agitation also factor into determining whether or not crystals form in a specific formulation.

Crystal formation in grained chewy candies can occur either by allowing the candy to crystallize on its own, with sufficient agitation during processing, similar to what is done in fondant, or by seeding the candy mass through addition of fondant or icing sugar, similar to what is done with fudge. The sucrose to glucose syrup ratio is critical to give the desired effect. If graining is to be done in the process, the sucrose to glucose syrup ratio should be sufficiently high to provide a supersaturation sufficient for crystallization. The nucleating ability of intense agitation is also often needed to initiate graining in the batch. If fondant or powdered sugar is to be added to set the grain, the sucrose to glucose syrup ratio can be lower, ideally such that the continuous phase is just saturated with sucrose when the fondant is added. In principle, all of the sugar crystals from the fondant then should remain intact (neither dissolve or grow), although in practice some crystal growth is generally the case.

11.4.1.1.4 Lipid Emulsion

In nougat and chewy candies, about 5–8% fat is added to reduce stickiness and enhance lubricity. Melted fat is typically blended into the warm candy mass under agitation to emulsify the fat through the sugar matrix. If emulsifiers were used in the formulation, they would migrate to the oil/water interface to coat the fat globules and help isolate the fat from the aqueous phase. The size of the fat globules and their dispersion throughout the candy depend on the extent of agitation. However, typically fat globules migrate to the air/water interface, a phenomenon well-known in ice cream and whipped cream. Fat globule migration to the air interface may not occur so readily in nougats due to the high viscosity of the continuous phase.

Figure 11.12 shows two views of fat globules in a sample of commercial nougat. At lower magnification, fat globules can be seen distributed throughout the continuous phase (aqueous sugar solution), although some preference for fat globules at the air/water interface can be seen. At higher magnification, fat globules can clearly be seen as the very small droplets dispersed throughout the continuous phase. The larger globular shapes are air cells. The circular arrangement of fat globules evident in Figure 11.12b was thought to be due to fat globules that coated the interface of an air bubble interface that no longer existed.

11.4.2 Physical Properties

The physical properties of aerated confections are governed by numerous factors, including (1) water content, (2) air content, (3) stabilizer type and content, (4) sugar phase (grained, ungrained, viscosity, etc.), (5) lipid content and arrangement, and (6) presence of inclusions. As with most confections, water content has a direct impact on hardness of aerated confections, with lower water content giving harder candy by raising the glass transition temperature (T_g) (see Section 2.9). Based on the relatively pliant texture of aerated candies, T_g must be substantially below 0 °C (32 °F), although the exact value depends on both water content and the composi-

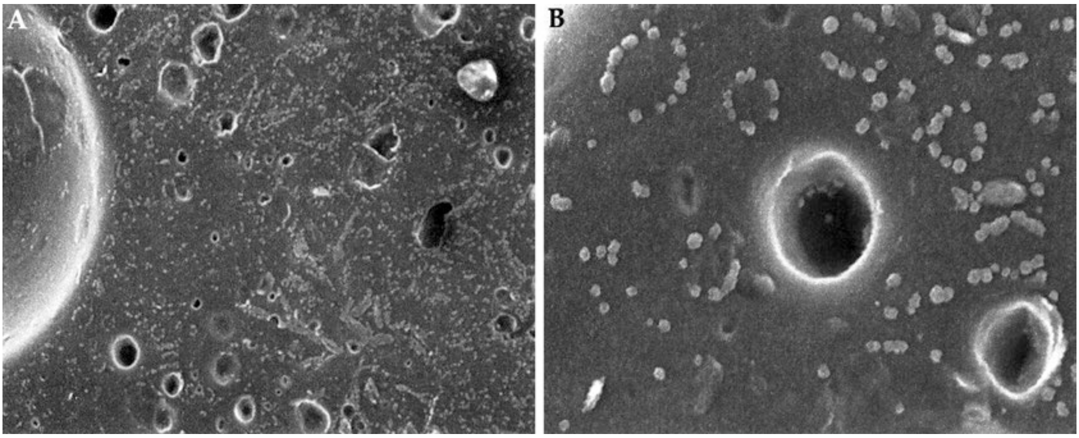

Figure 11.12 Scanning electron microscope images of fat globules in nougat: (**a**) low magnification; (**b**) high magnification (From Ziegler and Decker (2002), with permission)

tion of the continuous sugar phase. T_g of a commercial chewy nougat product (unspecified water content) was measured to be about −14.4 °C (Ziegler and Decker 2002). For marshmallow, T_g was measured as function of water content by Lim et al. (2006). When water content was 19.5%, T_g was about −45 °C, but that increased to 2 °C when water content was as low as 8% (Figure 11.13). It is this increase in T_g that, in part, causes dried marshmallows to have a harder texture.

Likewise, the presence of sugar crystals, emulsion droplets, and other particulate inclusions can break up the continuous phase and give a shorter texture to aerated confections. These components also increase stand-up quality and reduce cold flow.

Unique to aerated confections, though, are the effects of air and stabilizer on the textural properties. Of particular importance is how air and stabilizers influence the elastic properties of the confection. Both the amount of air incorporated and the nature of the air dispersion, specifically whether the bubbles are distinct, separate entities (closed cell) or whether they interact to form a network structure (open cell), have an important impact on physical properties. Furthermore, the nature of the stabilizer at the air interface and its inherent elastic properties also contribute to the viscoelastic response of aerated confections. However, very few scientific studies have investigated the effects of these factors on product attributes. Two of those studies will be briefly reviewed here.

The elastic properties of two commercial marshmallow products were investigated by Kaletunc et al. (1992). The marshmallow products were subjected to repeated compression and relaxation (decompression) cycles to investigate their elastic response. Not surprisingly, marshmallow exhibits viscoelastic properties in response to applied forces. When compressed, marshmallow may spring back to nearly its original shape, demonstrating elastic behavior. However, when subjected to repeated compressions, with or without a relaxation time (for recovery), the gelatin loses its elastic properties, resulting in a marshmallow that becomes increasingly shorter and more compact, with an increase in its apparent stiffness (modulus). Slight differences were observed between the two commercial marshmallow products studied, but no connection to the actual marshmallow microstructure was made.

Aerated confections also respond to tensile forces (stretching the candy apart) as anyone who has pulled a marshmallow apart in their hands can attest. The effects of specific gravity (from 0.66 to 1.1) on tensile properties of nougat were studied by Decker and Ziegler (2003). To produce nougat with different specific gravity, different levels of frappé were added to the cooked

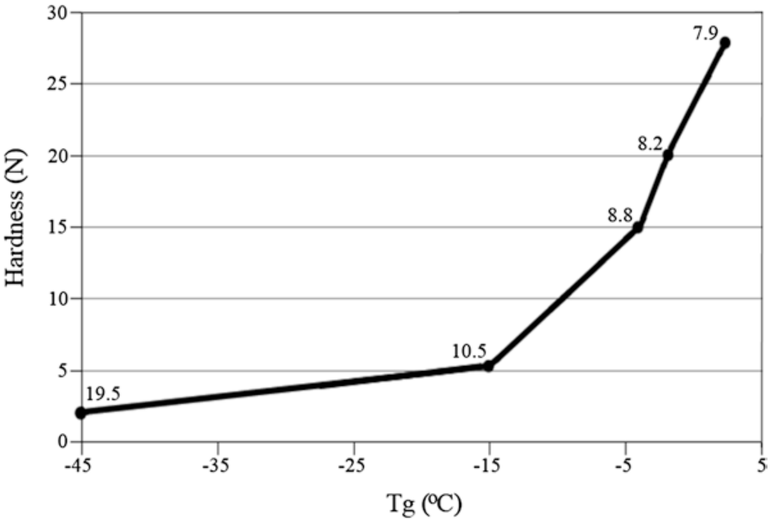

Figure 11.13 Hardness of marshmallow based on glass transition temperature (T_g) (Redrawn from data of Lim et al. (2006)) (Reprinted from Ergun et al. (2010) with permission). *Numbers* with each point indicate water content

sugar syrup, meaning that the amount of egg albumen (used for the frappé) also varied with specific gravity. Thus, differences in tensile forces documented were due to the combined effects of air incorporation and stabilizer level in the nougats. As specific gravity increased (less frappé added, so less aeration), the tensile modulus increased exponentially; in addition, penetration modulus and cutting force also increased exponentially over the same conditions. These results document the increasing effect of the dispersed air phase on physical properties of nougat. More air results in a product that is easier to chew and cut (than a similar sugar matrix with no aeration).

11.4.3 Shelf Life

Probably the main issue with reduced shelf life in nearly all classes of aerated candies is moisture loss during storage. A reduction in water content leads to hardening or toughening of the product. The ERH of aerated confections varies from as low as 0.4 for dried marshmallows to as high as 0.75 for the softest products with highest water content (Ergun et al. 2010). Under ambient conditions where relative humidity is less than 50%, there is a driving force for moisture to move from the candy to the air. Packaging layers help to retard water migration, but over time these candies will eventually lose moisture and become harder.

The loss of moisture from marshmallow to air was measured by Lim et al. (2006), who also correlated the changes in hardness and glass transition temperature, T_g (see Section 2.9). As seen in Figure 11.14, the marshmallow decreased in moisture content from an initial value of 19.5% to as low as 7.9% after 20 weeks of storage exposed to air at 21% relative humidity and room temperature. A significant increase in hardness also occurred over that time. The increase in hardness correlated to the increase in T_g, as shown previously in Figure 11.13.

Other changes that can occur in aerated confections relate to changes in either pressure and/or temperature during storage. The air within the candy obeys the ideal gas law so that any changes in ambient pressure cause changes in volume of air cells. For example, a decrease in pressure causes a subsequent increase in volume of the air cells (assuming temperature remains the same). The expansion caused by reduced pressure may cause problems, especially when the candy is not tightly constrained. For example, the change in air volume caused by shipping chocolate-coated nougat or marshmallow by truck across the mountains may cause cracking of the chocolate coating and result in unacceptable product.

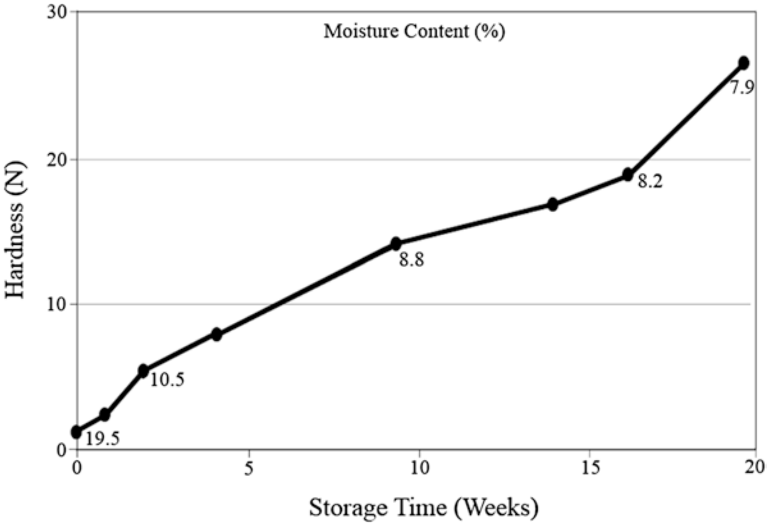

Figure 11.14 Changes in hardness, as correlated to moisture content, in marshmallow stored at room temperature and 21% relative humidity (Redrawn from Lim et al. (2006))

Furthermore, since proteins are not perfectly elastic, when marshmallows are shipped over mountains and then return to sea level, the gelatin does not return to its initial elastic state (as documented by the Kaletunc et al. 1992 study). Even though the decreased pressure causes an initial expansion of the marshmallow, the return of the marshmallow to sea level causes the marshmallow to collapse. Thus, maintaining careful control of ambient pressure is important to extending product shelf life for aerated confections.

Another issue during storage relates to the thermoreversible nature of the gelatin gel network. Typically, the melting point of gelatin in marshmallow candies is about 40 °C (104 °F). Storage above the melting point leads to the loss of gel strength and increase in fluidity. This can result in collapse of the air cell structure and loss of volume in the marshmallow. Thus, marshmallow products should be stored at cool conditions, well below the melt point of gelatin.

11.5 Troubleshooting

Some of the problems associated with each type of aerated confection cross the different categories, but some problems are specific to the type of candy and manufacturing process.

11.5.1 Improper Density

If specific gravity is different from that expected, the causes may either be related to the formulation or the process. Control of specific gravity of confections requires careful control of the aeration process, although each method of aeration generally has different control points. Batch pulling of chews or taffy is highly variable, depending on the operator for a decision point as to when the candy is sufficiently aerated. The frappé method of nougat manufacture relies on proper density of the whipped frappé plus proper ratio of frappé and cooked sugar syrup. Continuous aerators have high reproducibility because the exact ratio of air and sugar syrup can be metered into the enclosed chamber.

One potential reason that density of aerated confection might be higher than expected is that the stabilizer has been improperly hydrated, denatured or degraded. To be fully effective, any dried stabilizers need to be completely hydrated prior to use. If not, they will not support as much air incorporation. Also, heating proteins to excessively high temperature may cause denaturation (egg albumen, whey proteins) or degradation (gelatin) and lead to a decrease in their aeration capacity. Another potential cause for high density (low aeration) is that fat was added too early or overmixed, which caused collapse of air bubbles.

11.5.2 Product Too Hard or Rubbery

The primary reason for hard aerated confections is most likely related to moisture content. Depending on the candy, this might be seen as candy that is too stiff (nougat, grained marshmallow, chews and taffy), or tough and rubbery (ungrained marshmallow). Taffy that is too hard to eat is one of the main consumer complaints.

There are a number of potential causes for the water content of an aerated confection being too low. Cook temperatures that are too high is a possibility, either caused by inattention to the process conditions or from having thermometers out of calibration. However, water loss can also be caused during certain aeration processes (e.g., atmospheric planetary mixer), particularly if the environment is dry or if whipping is carried out for too long. Also, starch-deposited marshmallows can dry too far and become hard and rubbery if left in the starch for too long.

Other reasons for having hard or rubbery texture include (1) improper sugar formulation and (2) improper stabilizer selection. Using a higher DE glucose syrup or adding a humectant can help offset a hard texture. In marshmallow, a tough and rubbery texture might be related to the choice and amount of gelatin used. Reducing gelatin content leads to a softer, less rubbery, texture.

11.5.3 Product Too Sticky

Simply by their nature, aerated candies tend to be stickier than most candies. A coating of corn starch or sanding sugar is typically applied to marshmallow to prevent stickiness. Often, a sticky product is due to high moisture content, although it may also be related to sugar composition and fat content (nougats, etc.).

Candy with undesirably high moisture content is most likely due to improper cook temperature. For example, removing the candy mass from the cooker prematurely will leave excess water in the candy mass and lead to stickiness. As noted before, thermometers must be calibrated to ensure proper cook temperature. High moisture content can also occur when hydrated stabilizer is added back to the cooked sugar syrup; for example, improper water content of the stabilizer blend would lead to candy with high moisture.

Stickiness can also be caused by improper sugar composition, one with too many low-molecular weight sugars. One possible cause of this is excessive inversion of the sugar syrup during cooking. Using a lower DE glucose syrup or removing excess humectant can offset a sticky texture. Fat in nougats, chews and taffy is added to help prevent stickiness to processing equipment, packaging wrappers and teeth during consumption. Sufficient fat must be used in the formulation to provide the appropriate texture and further, the fat must be distributed homogeneously, in the form of small fat globules, throughout the candy mass to prevent stickiness. Finally, products can become too sticky (or hard) if improper barrier packaging materials are used or not sealed correctly. Candy that is not properly packaged can have moisture changes due to the environmental relative humidity.

11.5.4 Graining During Storage

Excess crystal formation in aerated confections can lead to undesirable changes in texture and appearance. Generally, graining occurs when the sugar matrix is too highly supersaturated. When the ratio of sucrose to other sugars (glucose syrup, invert sugar, etc.) is too high, or graining factor is too high, crystallization is promoted. Higher graining factors indicate higher crystal content and perhaps excessive shortening of the texture. Proper reformulation may be necessary to inhibit excess graining. A low water content can also lead to excessive graining as the sugar phase would be more highly supersaturated, although very low water content generally tends to inhibit graining due to the limited molecular mobility.

Graining may also occur if the crystalline sugars are not fully dissolved prior to boiling. There should be sufficient moisture in the premix (16–20%) to allow sugars to be dissolved before boiling occurs. Further, the sides of a batch cooker should be washed down after a full boil has started to prevent the splashing syrup from drying and graining, and then dropping seed crystals into the boiling batch. If the boiling mass is not above the scrapers, graining may also be induced.

11.5.5 Mold Growth

Although highly unlikely, mold growth may become a problem in ungrained marshmallows, particularly if the water content is too high and there are insufficient low molecular weight sugars to reduce water activity. Osmophilic molds are known to grow in systems with water activity as low as about 0.65. If a marshmallow product is formulated with a higher water activity, it is prone to mold growth. Reformulation to reduce water activity may be necessary. Addition of humectants (glycerol, sorbitol, invert syrup, etc.) may be required to retain a softer texture in candy with low water activity. Good sanitation practices for processing equipment, including drying starch if used, will also help prevent contamination before packaging.

11.5.6 Weeping

Marshmallow exposed to temperatures above the melting point of gelatin may weep, or exude sugar syrup, since the melted gelatin molecules are no longer capable of providing a network to hold the viscous sugar matrix. The melting point of gelatin depends on the gelatin source (fish being lower) and bloom strength (higher bloom results in higher melt point).

At high temperatures, the sugar syrup phase also decreases in viscosity, further promoting flow and weeping. Maintaining low temperatures during storage and distribution will prevent this problem. Use of a higher melting point gelatin might be an alternative, although the textural differences may be unacceptable. Higher levels of gelatin might also improve the problem. Sodium hexametaphosphate is thought to improve heat stability as well.

11.5.7 Shrinkage

Shrinkage and deformation of marshmallow is most often related to changes in the gelatin, but may also be caused by transportation under reduced pressures (e.g., over mountains) or storage at elevated temperatures (above 35–40 °C; 95–104 °F). Gelatin that has been excessively degraded during processing will not be as good at maintaining distinct air bubbles and can lead to shrinkage. High water content may also lead to shrinkage as can addition of fat-based ingredients.

11.5.8 Problems in Starch Deposited Marshmallows

When marshmallows are deposited into dried starch powder, moisture is lost from the product to the starch. This moisture loss is factored into the process design so that the candy after it is removed from the starch has the proper moisture content. For efficient drying, it is important that the molding starch has the right moisture content and be at the right temperature. If temperature, time and moisture content are not controlled, problems can occur that affect product quality. Typically, molding starch for depositing marshmallow should be at about 38–43 °C (100–110 °F) and moisture content of about 5–7%, depending on whether it is grained or not.

When the starch is too cold, the marshmallow in contact with the cold starch forms a sort of crust that inhibits further moisture loss from the interior and retards the drying process. The result is candy that is too soft in the middle with a harder crust layer. When the starch is too warm, a different problem occurs. The warm starch temperature causes loss of aeration and results in more of a jelly-like texture rather than an aerated marshmallow. If the starch is too dry, excess moisture loss can occur at the surface of the piece, potentially leading to a skin or crust formation while the interior of the marshmallow may be too soft (too much water). The texture and appearance of such a product are undesirable. Also, starch powder that is too dry is a risk for a powder explosion, which may be induced by a spark or heat source. If the moisture content of the starch is too high, the rate of drying is impeded and visible, discolored crust forms on the surface.

Surface crust formation may also occur if the water content of the marshmallow when deposited is too high. This can lead to rapid moisture loss from the surface and formation of a hardened layer. Depositing at solids content greater than 74% is necessary to prevent this type of crust formation. Finally the time the deposited candies are left in the starch must be consistent to provide proper moisture content and product texture.

11.5.9 Cold Flow

An amorphous sugar mass is prone to exhibit cold flow, where the candy spreads out either to fill a container or, if unbounded, to produce a puddle of candy. The microstructural elements (fat globules, air cells, protein networks, sugar crystals, etc.) are what provide stand-up properties to an amorphous sugar matrix. Thus, if any of these microstructural elements does not set up properly, even highly aerated confections can flow. This is particularly a problem with higher specific gravity confections like nougat, chews and taffy – without numerous stabilized air cells to prevent cold flow. Cold flow of salt water taffy, particularly in warmer temperatures, is a major concern. For this reason temperature control of product storage and transportation is critical.

Solutions to preventing cold flow are many, although not all solutions will work in a given situation. Probably one of the first approaches to resolve cold flow is to decrease the water content (cook to higher temperature). Less water means the amorphous sugar phase is more viscous and more resistant to flow. Unfortunately, lower water content also means a harder or tougher candy texture, something that may be undesirable in the finished goods.

Other approaches to inhibit cold flow involve manipulation of the microstructural elements. For a given specific gravity, more numerous and smaller air bubbles are better for stand-up properties than fewer and smaller bubbles. Thus, making sure that air bubbles are as numerous and as small as possible may help prevent cold flow. The same principle applies for fat globules – numerous small fat globules homogeneously distributed throughout the candy matrix provide the best stand-up properties. Using a fat with slightly higher melting point or solid fat content can also inhibit cold flow, although if the melt point is too high, there will be a waxy mouthfeel and loss of flavor notes. Some taffy manufacturers add intact corn starch granules after cooking, so that the particulate nature of the starch inhibits cold flow. Too many starch granules, however, also cause an undesirable short texture to the taffy. Inducing a fine grain in taffies and chews will prevent cold flow and provide a softer eating texture. Tight twist wrap packaging will by physical restraint help reduce cold flow.

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Jellies, Gummies and Licorices

12

12.1 Introduction

Gummies and jellies are a class of confections based on a hydrocolloid (sometimes called a stabilizer) that provides a network to hold relatively high moisture content sugar syrup. Licorices and licorice-like products mainly use flour as their source of stabilizer and for this chapter flour will be used in the same context as a hydrocolloid. The hydrocolloid gel also influences appearance, flavor release, and textural attributes. Traditionally, the term gummy (sometimes written as gummi) is reserved for candies made with gelatin, although this practice is not strictly followed around the world. Candies made with other hydrocolloids are generally called jellies. The most common hydrocolloids are gelatin, starch, and pectin. Each hydrocolloid imparts its own unique texture and organoleptic properties to the candy. Other hydrocolloids (such as agar, gum arabic, carrageenan, etc.) are often used in mixtures with other hydrocolloids to impart new characteristics and textures. Table 12.1 provides a comparison of various attributes of gummy and jelly candies based on different stabilizers.

Gummies, jellies and licorices typically have relatively high water content (16–20%), although hard gums may be as low as 7–8%. The physicochemical properties of these candies arise due to the cross-linking of the hydrocolloids into a gel. Individual hydrocolloid molecules bond together to form a network structure that traps the fluid sugar syrup within to give a semi-solid texture. The nature of the intramolecular bonding is dependent on the type of hydrocolloid, or their combination, used. In some cases, hydrocolloid molecules may be covalently bound through strong chemical interactions, whereas in other cases, the hydrocolloid molecules form a physical structure, without covalent bonding. Differences in bonding structures among the hydrocolloids are what impart the different textural attributes for the wide range of gummy and jelly confections on the market. Mixing hydrocolloids in gummy and jelly candies provides even greater variation in product texture due to the complex interactions in mixed, or composite, gels.

The setting rates and physical properties of the hydrocolloid candies are also dependent, to some extent, on the nature of the sweeteners used in the formulation since the sweeteners may impact gelation properties. Sucrose and corn syrup are the most common sweeteners used in gummy and jelly candies, but sugar-free versions based, for example, on maltitol and HSH can also be found. Glucose or even fructose, in combination with corn syrup, can be used as well. In general, the presence of these sweeteners raises the melting point of the gel and impedes gel formation, although this is not always true. For example, high sugar solids are required for certain types of pectin to form a gel.

To make jelly candies, sugar and corn syrup are typically mixed with the hydrocolloid and

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Table 12.1 Attributes of various hydrocolloids used in gummy and jelly candies

	Starch	Gelatin	Pectin	Agar	Gum arabic
Usage level (%)	10–30	6–10	1–2	1–2	20–50
Setting temperature (°C)	20–35	30–35	75–85	35–40	20–35
Setting time (hr)	12	12–16	1	12–16	24
Appearance	Cloudy, opaque	Translucent	Clear	Mostly clear	Translucent
Texture	Soft to firm, chewy	Elastic, firm	Short, tender	Short, tender	Very firm, hard
Flavor release[a]	Medium	Slow	Rapid	Rapid	Slow
Combinations with	Gelatin, pectin, gum arabic	Pectin, starch, gum arabic	Starch, gelatin	Starch, gelatin	Starch, gelatin

Adapted from Carr et al. (1995)

[a] Dependent somewhat on hydrophilic nature of flavor molecules

[b] High methoxyl (HM) pectin

cooked to the set temperature to give the desired water content. In starch-based jellies and licorices, cooking leads to gelatinization of the starch granule and subsequent cooling allows gel formation. The majority of pectin-based jellies are made by heating the sugar syrup in the presence of the hydrocolloid, with acid added just prior to cooling to induce gel formation at low pH. To make gelatin gummies, the sweeteners are often cooked separately from the gelatin, since gelatin is very heat sensitive. A hydrated gelatin solution is added to the concentrated sugar syrup after the syrup has been allowed to cool, and the mixture is then cooled to solidify into a gelatin gel matrix. The excessive heat, especially in batch cooking, causes the protein to degrade, losing some of its desirable gel properties. With continuous cookers, solubilized gelatin solution may be added prior to cooking the syrup with only minimal degradation due to the short cooking times and relatively low cook temperatures.

Once the sweetener and hydrocolloid solution has been cooked to its final water content, colors, flavors and organic acids are typically added prior to forming. Methods of forming can vary quite widely depending on the candy. Probably still the most common method of forming gummy and jelly candies is by depositing the fluid candy mass into impressions made in dried corn starch in a starch mogul and allowing the candy to set in the drying starch. However, starchless molding can also be used for forming certain jelly candies. Some jelly candies, like pectin candies, may still be slabbed and cut. Extrusion processing may also be used in certain applications for forming jelly candies and licorice production. Once the candies have dried and set into the desired conditions, they are generally given some type of finishing process. Sanding with sugar, panning, and oiling are common types of finishes.

12.2 Formulations and Ingredients

Gummies, jellies and licorices are relatively simple confections containing sweeteners, hydrocolloids, colors, flavors and, sometimes, organic acids.

12.2.1 Sweeteners

Sucrose and glucose syrup form the bulk of most gummy and jelly candies. They provide sweetness and body in the form of a colored, flavored sugar syrup that is held in place by the hydrocolloid gel. Sucrose content is generally about 40–50% of the sweetener solids (dry basis) since these candies should not grain. In general, the high residual water content and high glucose content in gummies and jellies (15–20%) means that the sucrose remains completely solubilized and does not grain.

Glucose syrup generally makes up 50–60% of the sweetener solids (dry basis). Typically, either 42 or 63 DE glucose syrup (or some combination) is used. The choice of glucose syrup is based on the desired characteristics of the finished candy since it can influence texture, sweetness, flavor release and shelf life. Use of higher DE glucose syrup leads to softer candy with lower water activity, but one that may be prone to stickiness.

For licorice candies, molasses may be added to the glucose/flour blend for flavor and color contribution. Fruit-flavored flour-based candy products generally do not contain molasses since this would offset the fruit flavors. Glucose syrup is usually the main sweetener for these candies with sucrose sometimes used to a lesser extent.

Various sugar-free versions of gummy and jelly candies can be found. Typical sweeteners used for sugar-free gummies and jellies include maltitol or sorbitol as the primary sweetener with maltitol syrup (or hydrogenated starch hydrolysate) added to prevent crystallization (in the same way that glucose syrup prevents crystallization of sucrose). Polydextrose may be used as a bulking agent in sugar-free gummy and jelly candies. Choice of sweetener is based on numerous factors, including caloric content, ease of use, and cost. Since most sugar alcohols are significantly less sweet than sucrose, a high intensity sweetener is often added. If added to the initial formulation, the high intensity sweetener must be able to withstand the high temperatures of cooking. Sucralose is often chosen for this reason.

12.2.2 Stabilizers or Hydrocolloids

Gummy, jelly and licorice confections cover a broad range of candies with different textural properties, primarily due to the type and amount of hydrocolloid employed. The type and nature of the sweeteners and the final water content also play important roles in determining product characteristics. The most commonly used hydrocolloids include starch, pectin, and gelatin, although gum arabic and agar can be used as well. Flour is used in licorice products. See Chapter 5 for specific details (chemistry, reactions, gelation mechanisms, etc.) of each hydrocolloid.

12.2.2.1 Starch

Starch is one of the most common hydrocolloids used in confections to produce a wide array of items from fruit slices to gum drops to jelly bean centers. Starch used in confections in the United States most often comes from corn, but other sources (wheat, tapioca, potato, etc.) can also be used. Starch granules are a semi-crystalline solid particle (1–30 μm) composed of amylose and amylopectin molecules (see Section 5.1). Starch at levels of 10–15% (dry basis) is added to the sweetener and cooked to cause complete gelatinization or complete loss of structure of individual starch granules; that is, most starch-based jellies contain only fragments of starch granules, with nearly all of the starch molecules dispersed into the aqueous phase. Sufficient water must be present during the cooking process to ensure gelatinization, although required water content depends on the type of starch, how it has been pre-treated (e.g., pre-gelatinized) and the cooking process. Lower water content is adequate for higher temperature (pressure) cooking methods, like steam injection (jet cooking), whereas higher water content is required for batch cooking and coil cookers. When using high-amylose starch, pressure cooking methods are required to provide sufficient energy to completely gelatinize the starch. Different types of starch, with different ratios of amylose to amylopectin or different modifications to the physico-chemical structure, give different textures in starch-based confections. Typical formulations for starch jelly candies are given in Table 12.2.

Most starch candies are relatively soft and easy to eat, although texture can vary quite widely (for example, the jujube is a hard form of a starch candy). Starch is also often used in fruit snacks. The nature of the starch gel and subsequent product characteristics can vary quite broadly and depend on such parameters as extent of starch gelatinization, ratio of amylose to amylopectin in the starch, nature of modifications to the starch granules, effects of sweeteners on gelatinization, and water content. Due to the nature of starch when it gelatinizes, the finished candy has a relatively opaque or cloudy appearance when compared with other gummy and jelly candies.

Table 12.2 Typical formulation (in %) for making sugar-sanded starch-based jelly candy (steam injection process)

	Starch jelly
Glucose syrup (62 DE)[a]	45–50
Sucrose	25–35
Water	9–14
Starch[b]	9–12
Acid	0.5–1.0
Flavor	0.25–0.5
Color	0.1–0.3

[a] Water content: 20%

[b] Thin boiling starch and high amylose starch

Table 12.3 Typical formulation (in %) for flour-based candy (licorice type)

	Licorice
Glucose syrup (42 DE)[a]	35–50
Wheat flour/starch	20–35
Sugar	0–15
Water	25–40
Oil	0.5–1.0
Acid	0.2–0.5
Flavor[a]	0.3–3.0
Color	0.1–0.3

[a] May be higher for black licorice with licorice extract and anise flavoring

Numerous modifications of starch have been developed to either enhance processing characteristics or moderate finished textural properties. For example, it is common to use so-called thin boiling starch for jelly candies that are deposited. This particular starch modification gives a cooked syrup a range of lower viscosities to allow easier depositing.

Most starch jellies are finished by sanding with sugar or given a soft-panned sugar shell (jelly bean). Some starch jelly products may be oiled to give a smooth surface appearance.

12.2.2.2 Flour

Licorice and fruit twist candies are the main category of confections based on flour, usually wheat flour. Wheat flour is often used in licorice products and similar fruit-flavored products at about a 30% level. When cooked, the partially gelatinized starch and denatured protein in flour form a chewy matrix with the sugars. Table 12.3 gives a typical formulation for licorice-type confections.

In the United States, there is a general misconception by the consumer that all flour-based chewy candies are called licorice, whether or not they contain licorice extract. Candy manufacturers, in recognition of the need for true licorice candy to contain licorice extract, typically label these flavored (fruit, chocolate, etc.) licorice-like products as fruit-flavored twists or something to that effect. Note that there are no regulations or Standard of Identity that governs the name licorice.

12.2.2.3 Gelatin

The firm, elastic nature of gelatin is a desired characteristic in the classic gummy (or gummi) bear candy. Gelatin, a protein derived from collagen, comes primarily from animal sources (cow, pig), although more recently fish gelatins have become available. Gelatin is generally used at levels of 5–10% in gummy candies to produce a firm, chewy gel. It is available in various bloom strength numbers. Bloom number is a measure of gel strength with higher numbers (e.g., 250) giving firmer gels than lower numbers (e.g., 125), at a given gelatin concentration. See Section 12.4.1.2 for more details. Some typical formulations for gummy candies are given in Table 12.4.

The texture of gummy candies can be manipulated in numerous ways (see Section 12.4.1.2 for more details). The nature (bloom strength) of the gelatin used, the gelatin concentration, the sweetener combination (i.e., sucrose to glucose syrup), and the water content are the primary parameters that affect properties of the finished piece. Based on the nature of the gelation process, gelatin forms clear gels. Gelatin forms a thermoreversible gel, meaning that gummy candies will lose their shape and structure if warmed above the melting point of the gelatin; thus, storage conditions are crucial for gummy candies.

Gummy candies are most often given a shiny appearance by finishing with wax dispersed in oil. Gummies can also be sanded with various grades of sugar or a mixture of acid and sugar for sour gummy candies.

Table 12.4 Typical formulation for batch-type gelatin-based candy

	Gelatin gummy
Glucose syrup (42 DE)[a]	37–42
Sucrose	31–34
Water (for sugar syrup)	9–12
Gelatin (250 bloom)	5.0–5.5
Water (for gelatin hydration)	9–11
Acid	0.6–0.9
Flavor	0.3–0.6
Color	0.05–0.1

[a] Water content: 20%

Table 12.5 Typical formulation (in %) for pectin-based candy

	Pectin jelly
Glucose syrup (62 DE)[a]	36–40
Sucrose	30–36
Water	20–25
Pectin (high methoxyl)	1.3–1.7
Sucrose (for pectin)	4–6
Acid	0.5–1.0
Flavor	0.3–0.5
Color	0.05–0.1

[a] Note that some confectioners prefer 42 DE syrup

12.2.2.4 Pectin

Pectin, a galactomannan hydrocolloid derived from fruits, is used in fruit slices and some types of jelly bean centers. The pectin used in confectionery jellies most often is extracted either from citrus peels or apple pomace and makes a firm gel at very low concentrations (1–2%). Pectin imparts a soft, tender mouthfeel, has a short break, and gives an extremely clear appearance. Table 12.5 gives a typical formulation for acid-set pectin jelly candy.

The most common form of pectin used in making pectin jelly candies is high methoxy (HM) pectin, meaning it has a degree of esterification greater than 50% (see Section 5.3). An acid (e.g., citric acid) must be added just prior to forming to set the pectin gel, which sets very quickly once the pH has been lowered sufficiently. Different modifications of pectin, based on either extent of methoxyl substitution or amidation, can be obtained that give different gel strengths. Low methoxyl pectin may be used in confections when a slower set time is required or an acid note does not fit the desired flavor profile.

Pectin jellies may be finished by enrobing in chocolate, sanding with sugar, or panning to give soft sugar shell.

12.2.2.5 Agar (Agar Agar)

An extract derived from certain types of seaweed, agar is a galactose polymer (or more precisely, a family of polymers) that forms a firm gel at very low (1–2%) concentrations. In confections, agar gives a short, tender gel that is easy to bite, very similar to pectin. Agar candies are also clear like pectin gels, and are often used to make sugar sanded fruit slices. Agar is also found mixed with other hydrocolloids to moderate texture. Due to the slow setting speed of agar, it is not widely used for jelly candies, although certain types of fruit slices may be made with agar as the primary hydrocolloid.

12.2.2.6 Gum Arabic (Gum Acacia)

Gum arabic (see Section 5.4.4) is the hardened sap of certain species of the acacia tree. A mixture of saccharides and glycoproteins, gum arabic has numerous applications in foods, from stabilizer to emulsifier. When used to make jelly candies, gum arabic forms a hard gel at levels of 30–60%. Gum arabic has been used to make hard gel cough drops, although its use in jelly candies is fairly limited. This is in part because of price volatility and cost for the relatively high usage level, but also related to difficulty in use (entrapped air).

12.2.3 Organic Acids

Organic acids are used to complement fruit flavors and to make sour jelly candies. About 1–2% acid (citric, malic, lactic, etc.) is added to the formulation, usually after cooking, to enhance fruit flavors and/or provide a sour eating experience. However, acids contribute to two negative effects in gummy and jelly candies. For example, the low pH and high temperatures as these candies are processed can lead to excessive degradation of gelatin and inversion of sucrose.

The rate of inversion of sucrose at elevated temperatures is enhanced when pH is reduced (see Section 1.3.1). The presence of fructose and glucose due to excessive inversion would lead to undesirably sticky candies and reduced elasticity in gummy candies. To minimize inversion, acid is added after the cook, ideally at lower temperatures, just prior to depositing. The formulation can also be buffered with sodium lactate or sodium citrate, which reduces inversion rate without influencing sour characteristics. For example, at 80 °C (176 °F) a sugar syrup (65°Brix) with 1% lactic acid has about 20% inversion of the sucrose in 20 min, whereas that level is reduced to less than 1% inversion when a buffered lactic acid systems is used. The use of a buffer salt provides the following benefits: (1) reduced inversion and thus, enhanced shelf life due to reduced hygroscopicity, (2) increased acid content without lowering pH, (3) reduced gelatin hydrolysis, improved gelatin strength, and less gelatin usage, (4) controlled gelling in pectin-based candies, and (5) reduced flavor variation.

Powdered or granulated acids may be used to sand jelly candies to enhance the sour eating experience. These are typically adding with sanding sugar during the finishing stages. Because these acids tend to be hygroscopic, the product needs to be dried to about 12–14% moisture to reduce moisture absorption.

The addition of acid not only provides flavor enhancement, it is specifically added to reduce the pH to cause high methoxyl pectin to set. In pectin jellies, the acid is added at the end of processing, just prior to forming. Once the pH is reduced, pectin sets into a gel very quickly so forming must take place immediately after acid addition.

12.2.4 Flavors

Flavor attributes depend on the type of gelling agent used and type of organic acid, if present. Liquid flavors, either water or oil-based, are most common for use in gummy and jelly candies. Typical usage levels for flavors in gummy and jelly candies are 0.1–0.2% for artificial flavors and up to 3% for some exempt from certification ("natural") flavors, although flavor levels may vary slightly based on the type of stabilizer used.

Table 12.6 Approximate composition of block licorice extract (Nieman 1977)

Component	Composition range (%)
Glycyrrhizin	15–18
Sugars	7–18
Gums and starch	19–42
Insoluble material	2–16
Ash	4–13
Water	12–17

In licorice candies, licorice extract, added at levels from 1.5% to 4%, provides much of the flavor. Licorice extract is an aqueous extract from the root of the licorice shrub. The primary ingredient is glycyrrhizin (or glycyrrhizic acid), a sweetener that is 50 times sweeter than sucrose. Black licorice extract composition is shown in Table 12.6, although exact composition depends on the region of growth and production methods (Nieman 1977). Licorice extract contains about 15–18% glycyrrhizin, although the characteristic licorice flavor comes from the hundreds of minor components also found in the extract. Anise flavor (aniseed oil) may be added to licorice candy to enhance and extend the licorice extract. Salt is also added as a flavor enhancer.

12.2.5 Colors

Typically soluble colors dispersed in water are used in gummy and jelly candy applications. In most cases, a concentrated solution of dyes is added after the cooking step, prior to depositing. The level of coloring agent to add depends on such factors as thickness of the piece, clarity, type of hydrocolloid and the method of finishing the piece (whether oiling, sugar sanding, etc.). Coloring material should be stable to the conditions they will be exposed to such as high temperatures and low pH.

In black licorice, caramel coloring may be used in addition to a black dye. Fruit twists containing no licorice extract are colored to match the flavor, as in red strawberry twists, a common confection in the United States.

12.2.6 Others

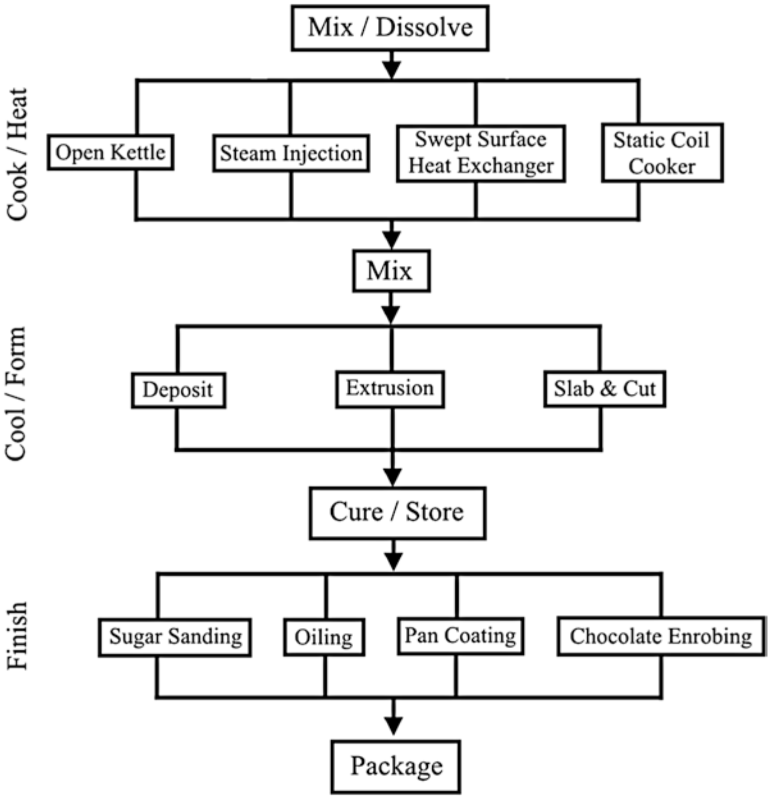
Many gummy and jelly formulations are now made with fruit juice concentrates to promote a healthier image. These concentrates provide sweeteners, and also provide colors and flavors.

In licorice and licorice-like fruit-twist products, various other ingredients may be added to moderate product characteristics. For example, a small amount of fat or emulsifier (typically monoglycerides) may be added to inhibit stickiness. A small amount (0.2–0.4%) of gelatin also may be added as a binder and to retain moisture. Various humectants may also be added to licorice and licorice-type products to retain moisture and texture.

12.3 Processing

The processes for making gummy and jelly candies vary slightly depending on the nature of the hydrocolloid used. They traditionally involve mixing the sweeteners together, either with or without the hydrocolloid, cooking the syrup to a set temperature to reach the desired product water content, cooling the syrup (and adding hydrocolloid where appropriate, along with colors, flavors and acids) prior to forming and finishing the end product. These steps are shown schematically in Figure 12.1. In some processes, however, the cooking step is replaced with a steam injection process to attain the final syrup for further forming. Formulation requirements are different between the two processes. Further, formulation and cooking requirements for licorice are different and distinct from gummy and jelly processing. As with most confectionery manufacturing

Figure 12.1 Schematic of processing steps for gummy and jelly confections



processes, numerous options exist for each of the steps, depending on the scale of operation and end product characteristics.

12.3.1 Gummies and Jellies

12.3.1.1 Dissolving, Heating and Cooking

The first steps in many gummy and jelly candy processing requires mixing the sweeteners followed by cooking the slurry to the appropriate temperature to get the desired moisture content. The aims of this part of the process are to make sure any crystalline sugars are completely dissolved, to solubilize the hydrocolloid (when appropriate), evaporate water, deaerate the syrup, and ensure the appropriate viscosity for the forming step. Several methods can be used for cooking of the sweetener mix for gummy and jelly candies, including batch kettle cooking, vacuum cooking, swept surface heat exchanger, and coil cooking. Extrusion cooking is often used for processing flour into licorice products.

The hydrocolloid (starch, pectin, gelatin, etc.) is typically heated with the sweetener, sometimes to induce the physico-chemical changes in the hydrocolloid that lead to gelation (i.e., starch). For gelatin gummies, hydrated gelatin is sometimes added to the cooked sweetener syrup after it has cooled somewhat to prevent denaturation of the protein. However, processes that use short cooking times often simply add the hydrated gelatin to the slurry prior to cooking. In many continuous cookers, the time at high temperature is sufficiently short that gelatin degradation is minimized (see Section 11.3.1).

The water content needed for cooking starch jellies is dependent on the type of starch used and the method for cooking. Starch granules require sufficient water to allow gelatinization, but this depends somewhat on the cooking conditions (e.g., pressure). When cooking at atmospheric pressure in an open kettle, the starch slurry must contain more water (up to 50% water) than when cooking in a pressure cooker (minimum 18% water) to ensure complete gelatinization.

The water content at the end of the cooking stage depends on the method of forming and the type of product. Typically, moisture content must be sufficiently high to give adequate flow (low viscosity) of the syrup for forming, particularly when depositing techniques are used. Typical water content for starch-based candies being deposited into dried starch is 20–25%.

12.3.1.1.1 Open Kettle Cooking

Cooking in an open kettle is the simplest method of preparing gummy and jelly candies. Either steam, electric heat or gas flame can be used to provide heat for cooking the sweetener and hydrocolloid (except gelatin) with an internal scraping blade to prevent scorching on the surface. The water content in an open kettle for cooking a starch slurry should be about 50% to ensure complete gelatinization. Due to the high water content and the long cooking time (30–45 min), open kettle cooking typically leads to significant browning of the sugars, which may cause off-colors in the finished candies. Also, there can be some restrictions to batch cooking of certain types of hydrocolloids. For example, high amylose starches cannot be cooked in an open cooker since they require higher temperatures to gelatinize. And, the extended cooking times can cause degradation of gelatin, which is why a hydrated gelatin solution is usually added after the batch-cooked syrup has cooled slightly.

12.3.1.1.2 Pressure Cooking

Pressure cooking is generally used to speed the cooking process, with elevated pressure meaning that higher cook temperatures can be realized. Increasing the pressure in the cooking process, whether in a batch kettle or a continuous cooker, increases the boiling point temperature and maintains the water in liquid form. This is particularly important for starch jellies since the starch has more time to gelatinize at high water content and temperature.

Pressure cooking can be accomplished in a coil (or static) cooker or a swept-surface heat exchanger. Extrusion cooking is also a form of pressure cooking. The steam injection process, while involving high pressures, does not evaporate water.

12.3.1.1.2.1 Coil (Static) Cooker

A static cooker is often used to heat and evaporate the liquid sweetener mixture for gummy and jelly candies. The static cooker is simply a metal coil contained within a steam chest filled with high-pressure steam. The sweetener slurry containing the hydrocolloid is pumped through the coil with condensation of steam on the outside of the coil causing rapid heating of the slurry. Steam condensate is continually removed from the bottom of the steam chest and either used for heat recovery schemes to recover valuable energy or returned to the steam boiler.

By use of a back-pressure regulator, pressure within the heating coil maintains the water in the feed slurry in liquid state despite the high temperatures. The residence time within the coil depends on the type of candy being made, although typical residence times are on the order of a minute or two. Once the super-heated slurry exits the back-pressure valve, the water is flashed off in an expansion chamber with the concentrated candy syrup exiting the bottom of the chamber, ready for further processing. Flashing off the water also helps to deaerate the sugar mass.

The static cooker is often used for gelatin because it gives a very rapid cook with minimal degradation of the protein (due to the short residence time) and minimal air entrainment. Thus, hydrated gelatin can be added directly to the batch prior to cooking, making this an efficient and convenient process for gummy candies.

12.3.1.1.2.2 Swept (or Scraped)-Surface Heat Exchanger

Another cooking method for jelly candies is the swept-surface heat exchanger (SSHE). The SSHE is comprised essentially of two concentric cylinders with flow of product through the interior and steam through the annular space. The starch slurry is pumped through the inner cylinder, which has an internal dasher with blades that either scrape the inside surface of the cylinder or come close to the surface (sweep the surface). The annular space between the two cylinders is where steam condenses to give the heating effect. Only a thin metal wall separates the condensing steam from starch slurry inside and this, in combination with the swept surface action, provides excellent heat transfer in the SSHE, particularly for viscous fluids like gelatinizing starch. Furthermore, since there is no contact between starch slurry and steam, the SSHE can be used for both heating and evaporation. Generally, the SSHE is operated under pressure to maintain water in the liquid state until cooking is completed, at which point the starch slurry enters a flash chamber to release the pressure and water is evaporated (flashed off).

Although the SSHE is an efficient cooker for viscous fluids, the relatively low surface area (for heating) and high capital costs limit its application in the candy industry to those where high viscosity is needed for subsequent forming steps. The SSHE is quite often used for cooking starch slurries and for continuous licorice manufacture (see next section on licorice processing).

12.3.1.1.2.3 Extrusion

Extrusion cooking is widely used in the snack food industry and can be used to manufacture licorice and starch gel pieces. Typically, a twin-screw extruder is used because of the advantages in flexibility in processing. In a twin-screw extruder, various operations, including mixing, cooking, kneading, release of vapors, and addition of minor ingredients just prior to forming in the die, can all be accomplished simply by careful selection of the screw elements. This flexibility has led to increased use of the extruder for various processes, including confectionery processing. For example, McHugh and Huxsoll (1999) studied extrusion of fruit/starch mixtures to form gelled fruit pieces. By controlling the temperature profile in the extruder (in six distinct zones), starch gelatinization could be controlled. They were able to produce gels having either completely gelatinized starch or with some ungelatinized starch and could thereby control texture of the resulting fruit gels.

12.3.1.1.3 Steam Injection Cooker

A common method of cooking starch slurries (sweeteners plus starch granules) for jelly candies is the steam injection cooker. The principle behind this process is shown in Figure 12.2. Steam injection cooking is also advantageous for processing gelatin slurries because the very short residence time minimizes degradation of the protein. The process also minimizes aeration of the gelatin candy mix.

In this system, high pressure steam is directly infused into a flow of the sugar slurry to provide rapid heat transfer as steam condenses directly into the solution. The amount of steam needed to condense depends on the input temperature (preheating), the type of slurry (heat capacity), and the end-point temperature. Typically, about 0.15 kg of steam are condensed per kg of slurry being processed, depending on the feed temperature, with all but a small fraction of that moisture flashed off upon pressure release. In some steam injection systems, this translates to about 1% increase in moisture content assuming an initial slurry solids content of 80%, pre-heated to 93 °C (200 °F) and cooked to 165 °C (330 °F). Preheating of the slurry is very important in determining how much water is condensed into the slurry. A rule of thumb would be that about 1% moisture is added to the slurry for each 5 °C (10 °F) of temperature below boiling point the slurry is fed into the steam injection head.

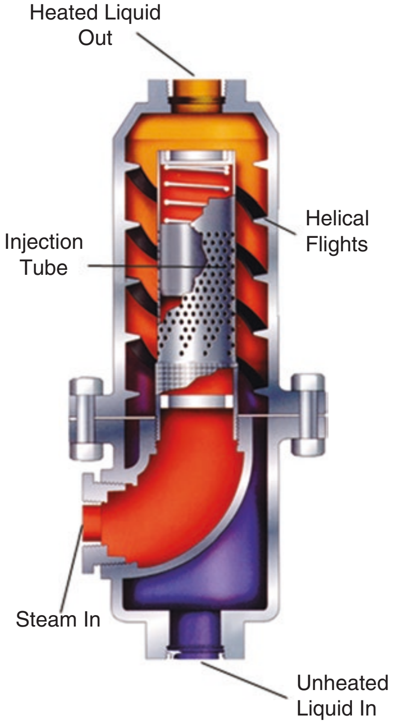


Figure 12.2 Principle of operation of steam injection cooker (Courtesy of Pick Heaters)

Steam injection quickly causes temperature of the slurry to increase as the pressure goes up. Between the rapid heat transfer and the shear forces within the mixing head, rapid gelatinization of starch granules occurs so that after just a brief (seconds) residence time in the injection cooker, the cooked starch slurry has been completely gelatinized. Most of the water that condensed from the steam in the mixing head is vaporized when the candy mass is released to atmospheric pressure. Again, the injection cooker does not evaporate water from the slurry; it only heats it up to promote starch gelatinization. Flashing water off after the depressurization valve also helps to deaerate the candy mixture, leaving a bubble-free candy syrup for depositing.

Another important point here is that the steam used in steam injection cookers must be culinary steam, meaning it is made from potable water and processed according to good manufacturing practices since it will be consumed along with the food. It must be free of any contaminants that might affect public health or food quality. Specific regulations apply to culinary steam. For example, additives used to treat boiler water (i.e., corrosion resistance, softening, etc.) must come from the FDA-approved list (see Code of Federal Regulations, Title 21, Chapter 1, Part 173, Subpart D, Section 173.310). Boilers, and the accompanying pipes and fittings, must also meet all food-grade processing surface requirements and equipment design standards.

12.3.1.2 Forming

There are numerous methods to form gummy and jelly candies into the final product shape. Probably the oldest and simplest method is to pour the hot syrup onto a cold table in a slab and cut the desired pieces from the slab. More often, though, the fluid candy syrup is poured or deposited into molds and allowed to solidify in the mold. Finally, some jelly-type candies and flour-based candies (licorice) are formed by extrusion.

12.3.1.2.1 Slab and Cut

One of the simplest methods of forming gummy and jelly candies is by pouring the hot candy mass onto a cool surface and allowing the mass to cool and solidify before cutting into the desired pieces. A candy batch may be poured onto cold tables (with cooling water circulating beneath the stainless steel surface), allowed to solidify and then cut into the desired shapes for further processing. Multi-layered candies can be made by sequentially layering candy syrups, although the bottom layer must be solidified before another layer can be poured on top. This process can also be made continuous by pouring the candy mass onto a cooling conveyor with solidification enhanced as it passes through a cooling tunnel. The solidified candy mass is then cut into the desired shapes for further processing. Rapid cooling can be achieved with the slab and cut method, but only a limited number of shapes can be formed.

Chocolate-coated pectin jellies may be formed and cooled by slabbing onto a cooling conveyor. Once the pectin has set, a series of knives and spacers cut the jelly into the desired shape and size and separate them for subsequent enrobing in chocolate.

12.3.1.2.2 Molding

One of the best methods to make candies with detailed shapes and patterns is by depositing the liquid candy mass into specially shaped molds. Molds can be made of plastic or polymeric materials, but quite often molds are made from dried starch powder (usually corn starch) shaped into the desired form. Once the candy has been cooled and dried (for starch depositing) to solidify, it is removed from the mold and finished prior to packaging. Most gummy and jelly type candies can be made by molding, although the rapid setting of high methoxyl pectin after acid addition makes it difficult to deposit these types of candies in traditional depositing equipment.

Modern depositing machines have wide ranging capabilities. Multiple depositors can be used to make several different flavors at the same time (good for mixed flavor bags), make multiple layers of candy in sequential deposits, inject a center filling within the primary candy deposit, and introduce unique colorful patterns (swirl, etc.) in a single deposit.

12.3.1.2.2.1 Starch Molding

Dried starch powder (usually corn starch, but may be wheat or another starch) makes an excellent molding material since it holds very fine details. The starch manufacturer adds a small amount (0.1%) of mineral oil or vegetable oil to the molding starch to ensure that candies retain excellent detail in the desired shape and to decrease dust release into the room. Properly prepared molding starch also removes some water from the deposited candy syrup, allowing depositing at higher moisture content (lower viscosity) than the finished good. Molding starch is also inexpensive, easy to work with and shapes can be quickly changed simply by replacing the press boards. However, dust can be a problem in manufacturing plants with starch depositing, and powder explosions are a continual concern. Starch molding has traditionally been used for forming gummy and jelly candies, although it is also used for forming a variety of other candies, including marshmallows, caramels and creams (see Chapter 9).

Careful conditioning of the starch is necessary for high efficiency operation. The starch must be at the proper temperature and moisture to hold the shape of the depression and be free from any contaminants or residual candies from previous batches. Table 12.7 provides typical target values for starch moisture content and temperature for each hydrocolloid. Gelatin gummy candies typically need lower temperature and water contents to prevent formation of a skin on the outside of the candy.

The general process of starch molding involves first filling a starch tray or board with conditioned starch and smoothing it off to make a flat, level surface. An impression is pressed into the starch with a form, or press board that has the desired

Table 12.7 Molding starch guidelines

Product	Moisture (%)	Temperature (°C)
Agar	6–8	35–46
		(95–115 °F)
Gelatin	6–7.5	26.7–35
		(80–95 °F)
Pectin	6–8	35–46.1
		(95–115 °F)
Starch	6–9	35–46.1
		(95–115 °F)

Figure 12.3 Depositing of jelly candy mass into a starch mold (Courtesy of Fast Track Engineering PTY, Ltd.)

candy shapes in multiple units. Hot cooked syrup containing the hydrocolloid is deposited into the depression (Figure 12.3) and allowed to cool and dry from several hours to 1 day plus. The fluid candy deposited into the starch typically has higher water content than desired in the final product in order to ensure sufficiently low viscosity so that the candy completely fills the mold, filling all the small points that give the desired detail. Once the candy piece has solidified (usually in a curing room) and is at the proper texture, the starch tray is overturned and the candy pieces separated from the starch on a screen. The candy pieces are cleaned of any remaining starch (e.g., using an air jet) and are ready for further processing or finishing.

The starch mogul is a continuous machine for performing each of the steps in the starch molding process, as shown schematically in Figure 12.4. It consists of several distinct zones: the tray feeding section, the starch buck (which empties incoming trays and prints new trays ready for depositing), the depositor, and the tray stacking section. At one end of the starch mogul, loaded candy trays from the curing room are input either manually or by automatic tray unloading onto the mogul conveyor. In the starch buck, the trays are overturned to unload the contents on a screen to separate candy pieces from molding starch. The candy pieces are removed from the screen and sent for further processing. The molding starch is sent to a drier to remove the moisture gained from the previous batch of candy and the dried starch recycled back into the mogul. Back in the mogul, the starch trays are righted, filled and leveled. Depressions are made in the dried starch by pressing the forms onto the tray as the trays continue moving through the mogul. The next step is depositing of the candy syrup into each of the depressions as the tray moves by on the conveyor. Often, the depositing nozzles move forward with the tray to ensure complete filling of each depression. At the end of each deposit stroke, the piston sucks back any residual candy syrup to prevent tailing. Careful synchronization of the depositors and starch trays is critical to proper filling. When operating at capacity, modern large (jumbo) starch moguls can process up to 35 starch boards (119 cm by 40.6 cm) per minute producing nearly 900 kg (>2,000 lb) of candy per hour. Once filled with candy syrup, the starch trays are removed from the mogul, placed on racks and wheeled into the curing rooms for solidification. Figure 12.5 shows a starch tray of filled gummy candies, ready for the next step in the operation.

12.3.1.2.2.2 Starchless Molding

Although starch makes an excellent molding material that is inexpensive and reusable, the various problems of working with starch (time required for curing, dust problems, potential for powder explosions, etc.) have led to starchless molding operations. In starchless molding, the hot candy syrup is deposited into a plastic or polymeric material with the desired shape, often with a small hole in the base to facilitate product removal. Since no drying takes place in a polymeric mold, the water content of the deposited candy must be that of the end product.

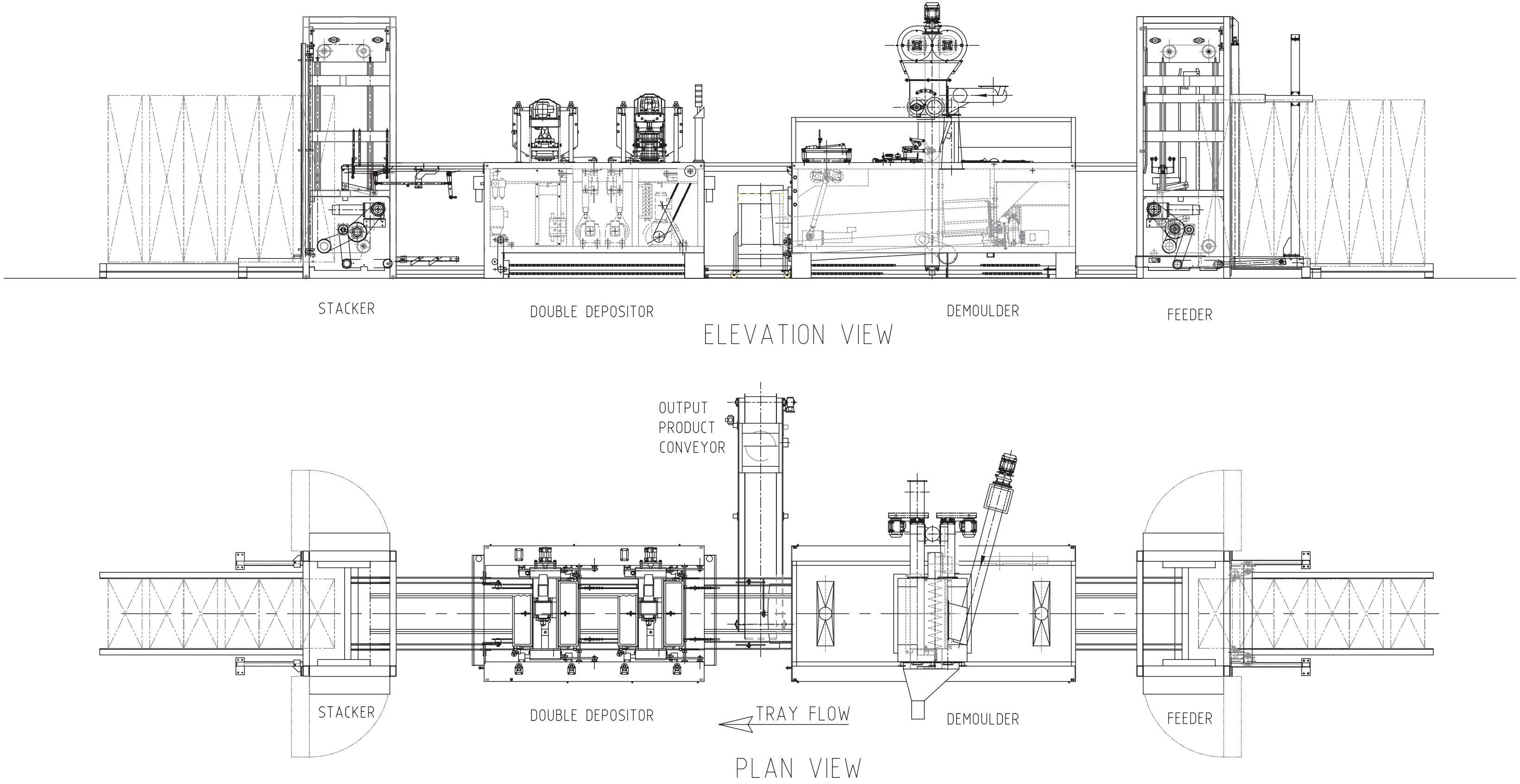


Figure 12.4 Schematic of a starch mogul operation (Courtesy of Fast Track Engineering PTY, Ltd.)

Figure 12.5 Starch tray filled with gummy candies (Courtesy of Fast Track Engineering PTY, Ltd.)

The candy in the polymeric mold is cooled to allow solidification of the gummy or jelly candy. To remove the solidified candy, the mold is overturned and the candy released from the mold by either tapping the mold from above, using a deformation roller to push the candies out, or applying a jet of air through the hole at the base of the mold. A release oil is typically needed to ensure proper release of the candy from the mold. The solidified candy falls onto a conveyor (also properly coated with release agent) and is then ready for finishing.

Due to the long setting times for most starches and gelatin, starchless molding is not often used for gelatin gummy and starch jelly candies. However, the rapid setting of pectin-based candy makes it a prime candidate for starchless molding, particularly if metal molds are used to enhance heat transfer rates. Cold-set starches may also be molded in this way.

Table 12.8 Curing room guidelines

	Temperature (°C)	Cycle time (h)
Agar	32–43 (90–110 °F)	8–24
Flour-based candy	40–50 (104–122 °F)	12–24
Gelatin	24–35 (75–95 °F)	8–24
Pectin	49–65.5 (120–150 °F)	8–24
Starch	49–65.5 (120–150 °F)	8–72

12.3.1.3 Curing (or Stoving)

The curing, or stoving, room is an important step in the gummy and jelly manufacturing process. Here is where the excess moisture in the candy is removed so the candy dries out as it cools and solidifies. Conditions in the curing room are important to proper solidification. With the exception of flour-based candies, relative humidity should be kept below about 50% in order to promote drying. Also, low humidity helps prevent the candy surface from getting sticky and the starch from picking up water (which will later have to be removed by drying). For licorice, relative humidity between 50% and 60% is generally used to prevent case hardening caused by lower RH.

Appropriate curing room temperatures depend on the candy type (Table 12.8). For gummy candies, temperatures must remain below the melting point of gelatin (between 30 and 35 °C; 86 and 96 °F). Higher temperatures are used for starch and pectin jellies to promote more rapid drying. Air flow must be sufficient to provide good heat and mass transfer to each of the trays. Often, a figure of 14.2 m^3/s (30,000 cubic feet per min) of air flow is recommended, but this can vary depending on room size and configuration. To ensure uniform drying of all trays, air flow must be carefully regulated so that the air flows across each tray uniformly. Dead spots, where air is not moving, can lead to excessively long curing times and inconsistent texture for candies in that area.

Curing rooms may be loaded and unloaded either manually or automatically. Large-scale automated systems often utilize computer control to track pallet movement from the starch mogul to the curing rooms and back again. These automated systems give highly consistent product as the candy moves through the curing rooms, but they are expensive and require more space than manual systems.

Because curing takes from 10 to 48 h (Table 12.8), the curing room is often a bottleneck in gummy and jelly manufacturing processes. That is, the speed of the cooking and depositing steps is much greater than that of the curing process; therefore, it is curing that generally limits throughput. The greatest throughput can be attained through proper choice of candy formulation to minimize curing times and by maintaining the best curing room conditions.

12.3.1.4 Finishing

Once the gummy and jelly candies have solidified, they must be finished in some way prior to packaging. If the candies have been deposited in starch, the first step in finishing is to clean the candy of any residual surface starch powder. After shaking out the starch trays, where the candies get caught on the separating screen and starch passes through, the candies are sent for further processing.

Typical finishing operations include oiling, sanding, panning and enrobing in chocolate. Prior to packaging, the candy pieces need to be equilibrated to packing room humidity to prevent moisture changes during distribution. Improper moisture equilibration can lead to products sticking together.

12.3.1.4.1 Sanding

Many starch, pectin and agar jelly candies are covered in coarse-grained, crystalline sanding sugar. These large sugar grains provide a stark textural contrast with the soft jelly center. The jelly candies are exposed to culinary steam to minimally wet the surface. The wetted candies immediately enter a rotating sanding sugar drum where they are tumbled with the crystalline sugar. The sugar grains adhere to the wet surface, which when dried leaves a uniform coating of sanding sugar on the surface of the candy. A second exposure to steam may be applied to smooth the surface and enhance the finish. A final drying step is needed prior to packaging to prevent sticking and microbial concerns. Often, the candy pieces are allowed to sit overnight to ensure complete moisture equilibration prior to packaging.

12.3.1.4.2 Oiling and Polishing

Most gummy, licorice and some jelly candies are coated with a layer of wax to provide a shiny appearance and to prevent pieces from sticking in the package. For example, gummy bears are typically coated with a thin layer of wax dissolved in oil to provide a shiny appearance. Fractionated fats, oils or waxes are applied to the surface of the candy as they tumble in a pan. Fats and oils used include mineral oil and fractionated coconut oil, among others. Beeswax and carnauba wax are commonly used waxes. Once the oiling layer has solidified, the candies are ready for packaging.

12.3.1.4.3 Panning

Many jelly candies are finished by putting a soft sugar shell around the piece in a process called panning. Jelly beans and fruit sours are common soft-panned jelly pieces. Application of a soft panned sugar shell is described in Chapter 13.

12.3.1.4.4 Chocolate Enrobing

Enrobing jelly candies with chocolate is not common, with the exception of pectin jellies. Typically, the enrobing process (see Section 15.6.2) is used to coat the candy piece in chocolate. Prior to enrobing, however, the surface needs to be completely dried to allow adhesion of the chocolate layer to the pectin jelly. Surface heating techniques, such as infrared radiation, are sometimes used to dry the surface without heating the entire piece. Once the surface has been prepared for coating, the jelly centers traveling on a conveyor pass first through a bottoming station, where a chocolate coating is left on the bottom of the piece, before passing through a curtain of liquid tempered, chocolate for a complete coating. The enrobed candy piece passes through a cooling tunnel to solidify the chocolate sufficiently for packaging.

12.3.2 Licorice

There are several different approaches to cooking licorice (Clark 1996; Cottam 2013; Veeramuthu 2017). The traditional batch method of cooking is still used in many facilities, although continuous cooking methods are also common. The entire process can now be accomplished in cooking extruders that mix ingredients, cook to the desired texture, and then form the candy, all in one process.

The traditional licorice process is a batch method, where ingredients are added to a pressure vessel and cooked. Sweeteners and other ingredients are added to the kettle with initial solids of about 60%, brought to a boil and cooked until the mass develops a “dull, mashed potato appearance” (Clark 1996). Some suggest that the flour should be added after the other ingredients are brought to a boil. Acids and flavors are added after cooking to prevent negative changes due to sucrose inversion or flavor loss, respectively. Conditions (temperature, sugar content, water content, pressure, agitation, etc.) must be controlled to attain the desired state of starch gelatinization in the candy mass. Here, complete gelatinization of the starch is not desired. Cooking may take several hours to attain the desired state, with solids content of about 70–74%. The candy mass is then cooled to allow formation of the gel network (starch and protein). To form the licorice, the candy mass is forced under pressure through a die plate with holes that give the desired shape of candy. The candy mass exiting the die of the extruder may be cut at the die plate into small, bite-sized pieces or collected in ropes on a conveyor and cut after cooling. Various shapes can be formed by choice of die, from solid ropes, to hollow tubes to star-shaped patterns. Candy is typically collected on trays for subsequent drying. Water content is reduced to from 18% to 20% in a dryer set at 40–50 °C (104–122 °F) and relative humidity of 50–60%. The dried product then goes on to packaging.

A slightly modified version of the traditional process eliminates the drying stage by cooking the batch directly to the desired water content of 13–15%. This candy mass is then extruded hot (no less than 70 °C; 158 °F) to form the desired shapes. If temperature is lower than this, it could be too hard to extrude. A filter prior to the extruder die helps to remove any flour lumps. The product exiting the extruder die is collected onto continuous cooling conveyors. After cooling, the product is then packaged. Elimination of the drying step greatly reduces the time needed for production; however, careful control of conditions is required to ensure the proper amount of starch gelatinization is attained.

Continuous methods of licorice production are also available. In one version, a pre-mix (18–24% moisture) is fed into a scraped surface heat exchanger (SSHE), where cook temperatures are about 121–127 °C (250–260 °F). The higher temperatures (than achievable in an atmospheric kettle) cause the desired level of starch gelatinization. Since the SSHE is under pressure, water remains liquid while within the system. Upon exiting the system to atmospheric pressure, some moisture flashes off, dropping the water content by 2–5%. The candy mass exiting the SSHE feeds an extruder (100–136 °C; 212–248 °F), which forces the mass through a die into the final shapes. After collection onto conveyors, the product is then cooled and ready for packaging. Production rates of 860–1,000 kg (1,900 to 2,200 lbs) can be produced in 2.5–3.5 h. However, hot production leaves a dull surface to the licorice. Gloss can be regained by passing the paste through a dilute alcohol-based shellac solution. Evaporation of the alcohol post-dip provides cooling.

Alternatively, a twin screw cooking extruder (operating at higher pressures and temperatures than the forming extruder used in the batch process described earlier) can be used to complete the entire process. A pre-mixed mass is fed into the extruder where cooking (and gelatinization) occurs in the first section, followed by mixing, cooling and then forming by pumping the warm mass through the die.

Prior to packaging, licorice is often treated to provide a unique surface appearance. If needed, the surface can be given a glossy appearance in a dip operation (as noted above). Some licorice may be oiled while other products are sugar and/or acid coated.

Sugar (or cream) pastes can be co-extruded with the licorice in a variety of shapes (sandwich, filled tubes, etc.). Cream pastes are highly crystalline candies with moisture content of 4–6%. They typically contain sucrose, glucose syrup, invert sugar, a small amount of fat, and gelatin to provide flexibility to the paste, along with colors and flavors. Multiple extruders making either licorice paste or cream paste(s) feed a complex die that co-extrudes the various shapes to create licorice allsorts.

12.4 Product Characteristics

Gummy, jelly and licorice candies owe their firm texture primarily to the nature of the hydrocolloid used and the water content. Gummy and jelly candies are essentially concentrated sugar syrup, with water content that varies from 10% to 20%, held in place by the network of the hydrocolloid gel. Lower water content leads to firmer candy. Hydrocolloid content may be as low as 1–2% for pectin or agar, or as high as 50% for gum arabic. The nature of both the hydrocolloid (type and concentration) and sugar syrup (sucrose to glucose syrup ratio, glucose syrup type, etc.) affects various attributes (texture, appearance, etc.) of these candies. Table 12.1 compares various attributes of the different hydrocolloids used in gummy and jelly candies.

There are many ways to study and characterize properties of these candies. Probably the simplest method of gaining information about texture is to press a probe (either flat or needle-shaped) into the gel and measure the force required to push the probe in a corresponding distance. Force-deformation curves provide unique information about gel characteristics, as seen in Figure 12.6. These curves show differences in texture of starch, gelatin and pectin gels. The gelatin curve shows a gel that responds with increasing force as deformation is increased, representative of an elastic gel. Pectin, on the other hand has a shorter and tender texture, with a fracture point evident at intermediate compressions. The starch gel, with a more chewy texture, exhibits a flat force-deformation profile. Once a limiting compression has been attained, no further increase in response force is observed.

The choice of analysis probe determines the characteristics of the gel being studied. A flat probe, as shown in the previous paragraph, typically indicates characteristics of tenderness. A needle probe penetrating a candy gel typically correlates best with chewiness. Stickiness can be

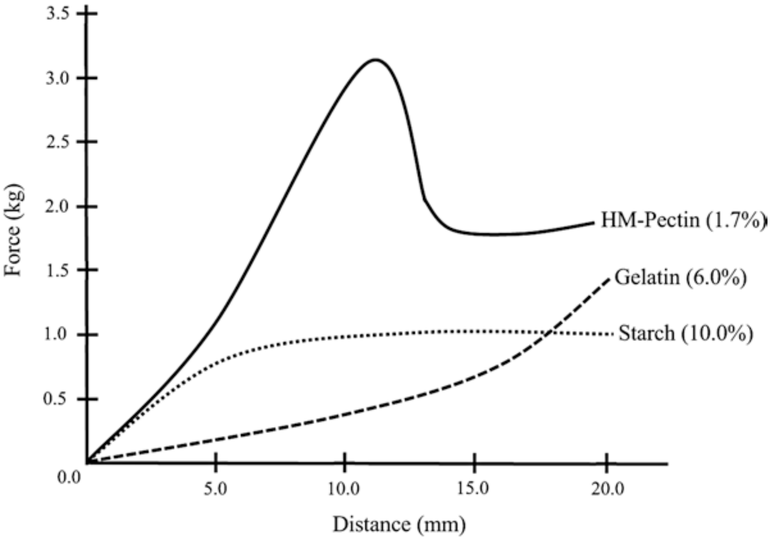


Figure 12.6 Typical force-deformation curves for different gummy and jelly candies

obtained by measuring the force required to pull the probe away from the candy piece. Alternatively, full texture profile analysis (TPA) can be conducted on the gelled candy by first compressing the sample to 75% of its initial height, releasing the compression while measuring adhesion forces and finally, compressing a second time to determine the amount of recovery of the gel. Depending on the shape of the force-deformation curve, parameters such as hardness, fracturability, adhesiveness, and springiness can be determined. More fundamental mechanical properties, storage (elastic, solid-like) and loss (viscous, fluid-like) moduli, can be determined for confectionery gels by using small angle oscillatory rheometers. However, small-angle oscillatory measurements do not deform the gel as done in the mouth during consumption, the correlation between storage and loss moduli and sensory attributes of a candy gel is generally not very high. Thus, large-scale deformation studies typically give better correlations with sensory measurements of physical properties.

12.4.1 Microstructure

Each hydrocolloid forms a gel with unique physico-chemical attributes and it is these attributes that lead to the differences in eating characteristics of the finished candy. The following section provides a brief introduction to the chemistry of gelation for the three main hydrocolloids used in confections. See Chapter 5 for more details on the chemistry of hydrocolloids used in confections.

To investigate microstructural aspects of confection gels, various microscopy measurements can be used (Groves 2003). Light microscopy can be used to investigate the larger structures (about 2–3 μm and above). The resolution of light microscopy can be enhanced when the samples are stained with dyes that improve contrast with specific components (e.g., proteins). The use of confocal scanning laser microscopy allows penetration of the surface to give a three-dimensional view of the structure, although resolution is still within the range of optical microscopy. To see finer details of the gel structure, electron microscopy, either scanning or transmission, is necessary. More recently, atomic force microscopy has been used to probe the molecular characteristics of candy gels.

Other methods to characterize the microstructural attributes of candy gels include differential scanning calorimetry (measures phase transitions) and x-ray analysis (determines crystallinity).

12.4.1.1 Starch Jellies

Starch granules heated in the presence of sufficient water go through several stages that lead eventually to formation of a gel structure. Starch granules contain two types of starch molecules, amylose and amylopectin. Amylose is a straight-chain polymer of glucose sub-units whereas amylopectin contains branched chains of glucose molecules. Both are arranged in a specific pattern within the starch granule, with amylose in amorphous form and amylopectin contributing to micro-crystalline regions. See Section 5.1 for more details on starch chemistry.

When heated, starch granules undergo several transitions depending on the type of starch, water content, temperature, and sweetener composition (Ratnayake and Jackson 2007). Although the exact steps in gelatinization are still a matter for debate and further scientific inquiry, the general steps are well recognized. First, there is a melting transition, where the micro-crystalline regions (primarily amylopectin) lose their crystalline structure. When starch granules are heated in the presence of sufficient water, they can also lose their identity in a process called pasting (Figure 12.7). In the early stages of heating, water begins to penetrate into the starch granule, causing the granule to swell as it hydrates. This swelling causes a significant increase in viscosity of a starch slurry. Further heating causes amylose molecules to leach out of the granule, leaving a ghost granule containing primarily amylopectin. There is a reduction in viscosity of the slurry at this point due to the extraction of starch molecules into the aqueous phase. Further heating causes complete pasting of the granule as the amylopectin molecules then become part of the

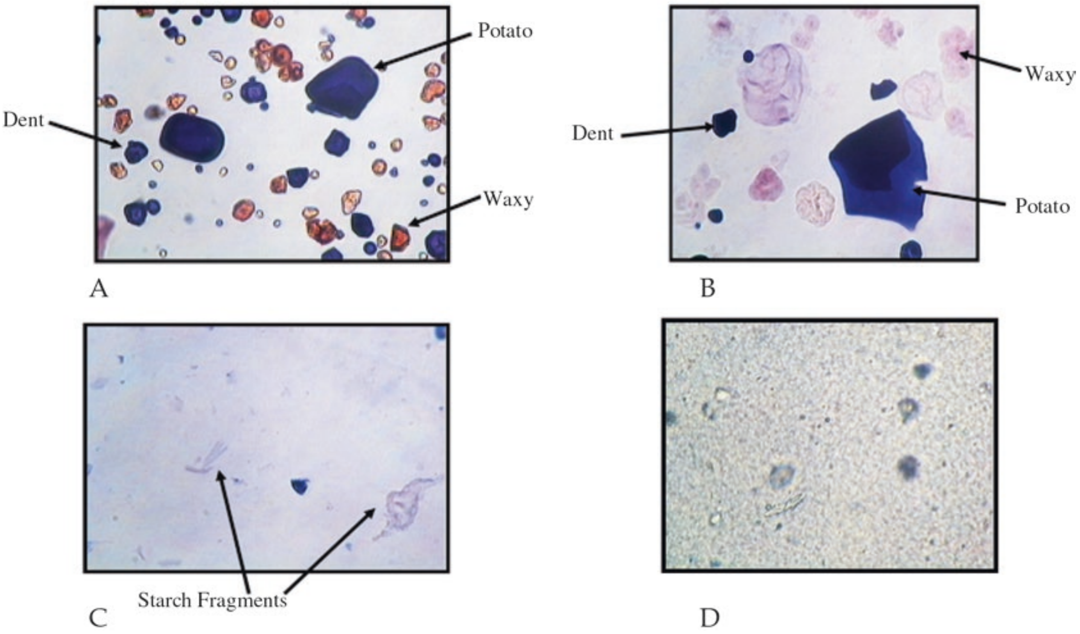


Figure 12.7 Starch gelatinization in jelly candy. (**a**) Intact starch granules; (**b**) Swollen granules; (**c**) Pasted granules; (**d**) commercial candy (Courtesy of M. Schwenk)

aqueous solution phase. In the presence of shearing, this process is enhanced and with sufficient levels of shearing (as in certain extruder operations or steam injection cookers), starch molecules can be broken down, or dextrinized, into polymers of smaller molecular weight.

Upon cooling, the individual starch molecules form a gel network that gives solid-like characteristics to starch jelly candies. In jelly candies, only fragments of the initial starch granules remain, whereas in flour-based candies (licorice), the number of intact starch granules remaining after cooking provides part of the unique texture of these candies. In both cases, it is the amylose molecules that have leached out of the granules that interact together to form a gel. A higher amount of amylose present in the initial starch granules leads to a firmer gel. The nature of these interactions among amylose molecules, amylopectin molecules and any remaining starch fragments gives a gel with an opaque appearance. Light does not pass through a starch gel structure.

The gel characteristics are dependent on such parameters as amlyose to amylopectin ratio, sweetener concentration and types, and water content. The presence of sugars during cooking of starch jelly slurries has several effects. First, the increased boiling point elevation of the sugars means higher cook temperatures can be reached (than in their absence), which leads to faster pasting at elevated temperatures. More significantly perhaps, though, is the effect of sugars on starch gelatinization itself. Generally, sugars provide somewhat of a protective effect on starch granules, increasing the temperatures necessary for pasting of the starch granule. The temperature at onset of gelatinization of starch in pure water is about 65–70 °C (149–158 °F), but that temperature increases to about 108 °C (226 °F) in a 50% sugar solution and 128 °C (262 °F) in an 80% sugar solution (Knoch 1976). For this reason, there may still be some partially-intact starch granules present in some types of starch jelly candies. In principle, this stabilizing effect of sugar on starch granules is related to the ability of sugar molecules to plasticize the starch granule (Perry and Donald 2002). Water is an excellent plasticizing agent for starch, and sugars have decreasing plasticizing ability with increasing molecular weight. Thus, the temperatures required for gelatinization of starch increase with increasing sugar concentration and increasing molecular weight of added sugars. Other theories abound to explain the effects of sugars on starch gelatinization (Sopade et al. 2004), including a reduction of available water for hydrating the starch granules, an increase in viscosity of the solution accompanied by a decrease in rates of diffusion, and specific sugar-starch interactions.

Amylose content is one of the most important attributes of the starch granule that impacts starch jelly properties, as seen in Table 12.9. Amylose is a critical component to forming a gel network because of its linear regions. Starch granules with only amylopectin do not form a gel upon cooling and the gel network strength, or firmness of the starch jelly candy, depends directly on the amylose content. The greater the amylose content, the firmer the gel and faster setting rate, for all other conditions being equal. However, high amylose starch requires high pressure cooking because of the tightly packed nature of the amylose molecules within the granule. Atmospheric cooking conditions do not attain sufficiently high temperatures to cause high-amylose starch granules to swell and paste.

Numerous chemical and/or physical modifications of starch can be performed to enhance its utility in various applications. In confections, the main modification to starch is an acid (or enzyme) hydrolysis that breaks down the starch molecules to smaller molecular weight (but not as small as maltodextrins). Because of the smaller molecular size, so called "thin-boiling starch" has reduced viscosity and higher fluidity at cooking temperatures, making it easier to fill complex mold shapes and reducing energy costs for pumping and depositing. Thin-boiling starch also has greater clarity and gel strength than untreated starch.

Many confectionery formulations use a combination of starches to take advantage of the benefits of each. For example, a mixture of thin-boiling (65–75%) and high-amylose (25–35%) starch is often used in jelly candies to provide reduced viscosity at depositing temperatures (thin-boiling) yet give rapid setting rates (high amylose) to minimize curing time. Other "quick setting starches" are available that can be used in place of high amylose starch.

Once the initial gel structure has been set during candy manufacture, changes in texture over time can occur due to rearrangements of starch molecules. The starch gel is a metastable state that rearranges over time to reduce internal energy. In particular, amylose molecules rearrange into a tighter, more crystalline structure in a process often called retrogradation. Retrogradation leads to firmer gels. Fortunately, sugar is a good inhibitor of retrogradation, so changes over shelf life of starch-based jellies due to retrogradation are not common.

Recent advances in starch modification technology now allow production of jelly candies without the need for heating. These starches have been instantized in the granule through the use of high temperature and pressure in an alcohol/water reactor. Addition of cold water causes swelling and thickening of these starches into a gel structure with textures dependent on extent of modification. Besides the type of starch modification, parameters such as type of sweeteners, water content and mixing temperature also influence the final state of the confections made with instant starch technology.

Table 12.9 Functionality of native and high-amylose starches

	Waxy corn	Tapioca	Potato	Dent corn	Wheat	High amylose	High amylose
Amylose content (%)	0	17	20	27	27	55	70
Gel characteristics	Non-gelling	Soft gel	Salve consistency	Firm gel	Soft gel	Firm gel	Very firm gel
Setting time	Does not gel	Average	Average	Average	Average	Rapid	Very rapid
Clarity	Clear	Clear	Clear	Slightly opaque	Slightly opaque	Cloudy	Cloudy

12.4.1.2 Gelatin Gummies

Gelatin is a protein hydrolyzed from collagen, the proteinacious material found in connecting tissues of animals. Due to its unique molecular characteristics, gelatin forms a gel with desirable characteristics in gummy candies. Gelatin chemistry is described in detail in Chapter 5.

Gelatin forms a thermoreversible gel, one that freely goes back and forth between a solution (sol) and a gel when temperature goes above or below the melting point. Above the melting temperature, the gelatin molecules are completely in solution (a sol), being completely hydrated as individual molecules (in a coil conformation). When temperature is reduced below the melting temperature, gelation occurs as the individual gelatin molecules cross-link, through a combination of hydrogen bonding, electrostatic interactions and hydrophobic interactions, to form a network. The nature of the gelatin gel depends on numerous factors, including other components that may be present (sugars, etc.) and processing factors (cooling rate, etc.). When temperature is increased again above the melting point, the gelatin molecules once again become completely hydrated in the aqueous solution.

The melting point of gelatin in a gummy candy depends on the type of gelatin used (primarily bloom strength) and the sugar content of the candy formulation. Melting point of gelatin varies from about 31 °C (88 °F) for 250 bloom gelatin to 28 °C (82 °F) for 100 bloom gelatin (as measured for a 10% gelatin solution). The presence of sugars raises the melting temperature slightly, with sucrose having slightly greater effect than glucose at equivalent molar addition levels.

Below the melting point, the sol-gel transition involves individual gelatin molecules forming a network structure as temperature is reduced. The individual gelatin molecules interact at junction zones to form a network within which is found the aqueous sugar solution of the gummy candy. Although the specific mechanisms of the sol-gel transition, or formation of the junction zones, are still a topic of current research, the general steps are fairly well understood based on studies done with rheology, light scattering, optical rotation (to follow triple helix formation), and atomic force microscopy. It is generally accepted that gelatin molecules go through a three-step process during gelation (GMIA 2012). The first step involves monomer aggregation, where individual gelatin molecules associate at specific sites on the protein molecule through various intermolecular forces, including hydrogen bonding. The second step involves the transition from the coil conformation in solution to a single-helix structure in the regions of intermolecular cross-linking. The final step is a transition from single to triple-helix interactions as the gelatin molecules attempt to transform back to the original state found in collagen, which leads to a strengthening of the gel network. The time scale of these steps is such that the initial gelation process occurs relatively quickly, over a period of minutes to hours (depending on conditions), while the final transition to the triple helix form may take weeks to be completely at equilibrium.

The nature of the gelatin network determines the physical attributes of the gummy candy. In general, gelatin forms a translucent gel with elastic properties dependent on the nature of the gelatin cross-linking. The number density and size of the triple helix junction zones determines elastic properties, with more and larger zones leading to greater elasticity of the gel. Both processing conditions and formulation of the candy affect the textural properties of the gelatin gummy candy through an influence on the rate of network formation and the subsequent strength of the molecular network. From a processing standpoint, thermal history and cooling rate can significantly affect gummy candy properties.

One of the most important steps in producing gummy candies is hydration of the gelatin. To ensure proper manufacturing, powdered gelatin must be completely hydrated prior to addition to the candy batch. Typically, powdered gelatin is mixed in excess water (nominal 1:2 ratio) for 0.5–2 h, depending on the gelatin particle size, to ensure complete hydration. Hot water, 80–90 °C (176–194 °F), with vigorous mixing is used to hydrate fine gelatin powder, whereas cold water (room temperature) may be used for coarser gelatin powders. Depending on the cooking process, the hydrated gelatin may be added either before or after the cook. If added prior to cooking the sugar syrup to the desired water content, the gelatin is prone to degradation, depending on the time and temperature profile during cooking.

Furthermore, compositional factors also significantly impact the properties of gummy candies. In particular, the type of gelatin used and its concentration significantly affect textural properties of gummy candies. Typically, lower bloom gelatin (150) is used at higher concentrations to produce candies that are softer, chewier and more elastic. Lower concentrations of higher bloom (250) gelatin, in comparison, give gummy candies that are more tender and short, but firmer in texture.

Bloom strength of gelatin relates to the hardness of a gelatin gel under standardized conditions. It is the weight required to push a 13 mm diameter probe to a depth of 4 mm in an aged (16 h at 10 °C) gel with 6.67% (w/w) gelatin. Higher bloom strength means that the gelatin molecules form a firmer gel. Due to the nature of molecular cross-linking, gelatin gives a firm gel with a high Young's modulus (initial force versus deformation, or stress versus strain), which correlates with bloom strength. Bloom strength is a function of the molecular make-up of the gelatin molecules, including average molecular weight and amino acid composition. A gelatin of one bloom strength may be replaced with another gelatin of different bloom strength to give the same gel firmness by changing gelatin concentration. Conversion charts are available for replacing one gelatin with another (Table 12.10). This is sometimes useful in commercial product development. For example, gelatin of 150 bloom strength can be replaced with 1.25 times as much 100 bloom strength gelatin to give a gel with the same firmness. Although these conversion tables are useful for matching bloom strength, other textural properties may be different. For example, the texture of a gummy candy made with 250 bloom gelatin is much shorter (breaks more easily) than that of an equivalent candy made with 150 bloom gelatin to the same gel strength (according to the equivalents shown in Table 12.10).

Table 12.10 Relative concentrations of gelatin of different inherent bloom strength to give a gel with identical bloom strength

Bloom[a]	100	150	200	250	300
100	1	0.80	0.68	0.58	0.51
150	1.25	1	0.85	0.73	0.64
200	1.47	1.17	1	0.87	0.76
250	1.69	1.33	1.16	1	0.88
300	1.90	1.45	1.32	1.13	1

[a] Replace gelatin in first column with equivalent concentrations of gelatin; for example, replace 150 bloom gelatin with 1.25 times as much 100 bloom gelatin to produce a gel with the same strength

Since the sol-gel transition of gelatin involves a change in hydration state of the protein molecules (Miyawaki et al. 2003), any additive that affects water activity (or water "potential") can influence gelation. Thus, sugars have a significant impact on gelatin gelation due to their effect on water activity in solution, especially at the high levels of use found in gummy candies. In general, the reduction of water activity with addition of sugars serves to help stabilize the gel state. The result is higher melting temperature and heat of melting. Sugars also help to stabilize gelatin during heating, mitigating the effects of temperature on degradation during cooking.

The type of glucose syrup used in gummy candy formulation also impacts textural properties of the finished piece, in part by influencing the setting characteristics of gelatin but also through its inherent properties. Use of a higher DE glucose syrup (62 DE) leads to candy that is more tender and less chewy, but increases tackiness (stickiness) of the product.

In proteins, pH plays a significant role in determining the charge distribution around the amino acids that make up gelatin. The isoelectric point, defined as the pH where there is no net charge on the protein molecule (positive and negative charges balance out), of gelatin depends on the extraction method used to process the initial starting material, collagen (see Section 5.3). Acid processing gives type A gelatin (typically porcine) with an isoelectric point, pI, between 6.3 and 9.5, whereas alkali processing gives type B gelatin (usually bovine) with a pI between 4.5 and 5.2. Finally, water content has a significant effect on hardness of gummy candies (see Chapter 3 for a general discussion about water in confection). Not surprisingly, as water content decreases (cook temperature increases), gummy candies become harder and firmer, with a more elastic, chewy characteristic. They also become less tacky at lower water content.

12.4.1.3 Pectin Jellies

Pectin, the methylated ester of polygalacturonic acid, is extracted from citrus peels and apple pomace. It is essentially a linear polysaccharide of D-galacturonic acid, although both molecular weight (from 50,000 to 150,000 Daltons) and molecular composition (substitution of other sugars like rhamnose in the polymer chain, degree of methyl esterification of the carboxyl group, degree of amidation, etc.) significantly impact gelation properties. Of specific interest in confections is high methoxyl (HM) pectin, where more than 50% of the free acid groups of galacturonic acid esterified with methyl groups (typical range is 60–75% esterification). Low methoxyl (LM) pectins have less than 50% esterification (typical range is 20–40%), and which may also have different degrees of amidation, and see only limited use in confectionery applications (particularly where low pH is problematic or a slower set time is required). See Chapter 5 for more detailed description of pectin chemistry.

Pectins are highly soluble in water although hydrating a pectin powder requires careful attention. To ensure rapid hydration of pectin, the powder is generally diluted with sugar crystals at a ratio of 1:5 or higher, which keep the pectin particles from aggregating as they initially swell up on moisture uptake. Alternatively, pectin can be hydrated with a high-shear mixing device to prevent particle aggregation.

The mechanism of gel formation depends on the type of pectin, with HM pectin being gelled by reduction of pH (addition of acid) and LM pectin being gelled by addition of calcium ions. Due to the speed of gelation, particularly with acid-set pectins, it is often relatively tricky to work with HM pectin in confectionery applications.

HM pectin forms a gel in concentrated sugar solutions upon acid addition. As pH is reduced, the carboxyl groups become deionized, reducing charge repulsion between the pectin molecules and leading to aggregation via a combination of hydrogen bonding at the acid or hydroxyl groups on adjacent chains and hydrophobic interactions between methyl ester groups. These associations may be considered junction zones, where pectin molecules are cross-linked, with the remaining part of the molecules still in solution. The pK_a value of 65% DM (degree of methyl esterification) pectin is about 3.55; however, gelation may occur at slightly higher pH, particularly for higher DM pectin. In general, a pH of 3.5 or lower is considered necessary for gelation of HM pectins used in confectionery applications. However, pH alone is not sufficient for gelation of HM pectin; total solids content, usually in the form of dissolved sugars, must be greater than 55% (but not greater than 85%) in order for gelation to occur. Sugar molecules compete for water, reducing the hydration of pectin molecules and making them more prone to gelation. The combination of low pH to reduce ionization and high sugar content to control hydration is necessary for gelation of HM pectin.

LM pectin sets via a very different mechanism than HM pectin, requiring the presence of a divalent cation for gel formation. In this case, the divalent cation, usually Ca^{++} or Mg^{++}, creates a junction zone between carboxyl groups on adjacent (parallel) pectin molecules in what is often referred to as an “egg box” association based on the presence of the cation between four galacturonic acid moieties (two per adjacent pectin molecule). Electrostatic bonds (free electron sharing) between oxygen atoms on the galacturonic acid moieties are responsible for the association among pectin molecules and gel behavior. Soluble solids content and pH have little if any effect on gelation in LM pectin. However, degree of amidation has a significant effect on gelling ability, with higher degree of amidation pectin requiring less calcium addition for gelation.

The nature of the gel depends on the type of pectin used. All pectin types make an exceedingly clear gel, with excellent clarity; however, the physical characteristics of the gel vary by pectin type. HM pectin creates a soft, tender gel that is much shorter (easily broken) than other hydrocolloids (except agar, see Table 12.1). LM pectin with high degree of amidation also forms a firm gel (a cut surface holds its edge) when pH is below 3.5, but has more rubbery texture than HM pectin. LM pectin with low degree of amidation does not form a firm gel, giving more of a preserve-like consistency that does not hold a cut surface.

Pectin is characterized by its gel strength, which is usually standardized to 150 USA-SAG. The method for standardizing pectin gel strength is based on the amount of "sag" experienced by a gel under standardized conditions. A pectin gel (1 part pectin and 150 parts sucrose) is made in a cup of specific dimensions under controlled conditions (65% soluble solids, pH of 2.2–2.4). The gel is allowed to set for a day at 25 °C before being upturned onto a measuring glass and put into a unit (the ridgelimeter) that measures height. The extent of sag of the pectin jelly is measured after 2 min. To give 150 SAG grade pectin, the gel should have fallen in height by 23.5% (height after 2 min 23.5% less than initial height). Pectin is standardized by adding sucrose to give consistent results.

Numerous factors affect both setting ability of pectin and the nature of the jelly candy. For HM pectin, the speed of gelation increases with the degree of methyl esterification. When DM is greater than about 70%, HM pectin sets very quickly, within a minute or two, making it somewhat difficult to work with in confectionery plants but allowing quick release after it has been molded. When DM is between 62% and 68%, HM pectin is considered to be "slow-setting"; however, even this grade sets up within 3–5 min. To slow setting times of pectin gels upon acid addition, buffer salts may be used to moderate acidity. Typically, sodium or potassium citrate are added as buffering agents to slow down gelling rate, although they can also impact textural properties. For example, potassium citrate leads to a more elastic but less firm gel.

12.4.1.4 Flour in Licorice and Licorice Type Confections

Flour, particularly wheat flour, is the most critical ingredient in licorice and similar products, making up between 25% and 40% of the composition. Flour contains about 70% starch with a significant amount of protein (gluten), about 15%, along with water (11–12%) and minerals. Although amylose to amylopectin ratios in starch can vary widely, wheat flour typically contains about one quarter amylose and three quarters amylopectin, both of which impact gelatinization during processing and final product texture.

Probably the most critical aspect of making licorice is controlling starch gelatinization. The characteristics of licorice under different conditions of starch gelatinization have been described by Knoch (1976). For licorice, a small amount of swollen starch granules is desired for a smooth, firm and chewy texture with a nice shiny appearance. If starch granules are not sufficiently gelatinized, meaning that numerous starch granules may be swollen but remain essentially intact, the resulting licorice product is firm and dry, with a spongy, bread-like consistency. If starch granules are over-gelatinized, meaning that all granules are completely fractured, the resulting licorice product is limp and elastic, with a tight, chewy consistency. Since free starch molecules do not hold water as effectively as swollen but intact starch granules, licorice that is over-gelatinized has a shiny appearance and is likely to be sticky, whereas under-gelatinized licorice has a dull appearance but can hold higher water content without becoming sticky. Although the gluten in the flour can also impact texture, the key to controlling the physical attributes of licorice is primarily related to governing the extent of starch gelatinization.

Numerous factors affect the extent of starch gelatinization in licorice products and thereby, influence characteristics of the finished candy (Knoch 1976; Jackson 1986). These include:

1. *The amount and nature of the flour used*. The amount of flour in a formulation significantly affects properties, with higher levels of flour

giving a firmer texture. The type of starch (amylose and amylopectin content/ratio) and gluten content of the flour used in licorice candy affect extent of gelatinization and thereby influence texture. The composition of the flour can also vary due to the variety of the wheat used and processing variables that will affect the starch/protein ratio. Flour may be modified by addition of starch (native or modified) to effect textural changes. As noted previously, the amylose to amylopectin ratio can significantly impact the nature of a cross-linked gel following starch gelatinization. Higher amylose content gives a stronger gel structure, although amylose levels that are too high may significantly retard gelatinization. Gluten also influences starch gelatinization. It is thought that gluten interacts (or complexes) at the surface of the starch granule to interfere with the hydration and/or amylose leaching out of the granule during swelling, thereby inhibiting gelatinization. Higher temperatures are needed for gelatinization in the presence of gluten.

2. *Water content during cooking and final water content*. Starch requires sufficient moisture to gelatinize; if it is cooked in the presence of too little water the starch does not gelatinize and will give a firm and dry texture, whereas excess water over gelatinizes the starch and yields a soft chewy consistency. As with all confections, final water content also impacts candy characteristics (appearance, hardness, firmness, chewiness, etc.), although this can typically be controlled independently of the cooking process.
3. *Sugar type and content*. The availability of water for hydration and gelatinization of starch during cooking is influenced by the nature of the sugar syrup. Water hydration of sugar molecules reduces the water molecules available for starch gelatinization, causing an increase in gelatinization temperature as sugar content increases. The molecular weight distribution of the sugar phase impacts both water availability (water activity) and boiling point temperature (see Chapter 3).
4. *Processing equipment choice and manufacturing conditions*. Process conditions, such as pressure, temperature, shear rate, cooking time, etc., have significant impact on starch gelatinization and licorice candy characteristics. Over the years, traditional cooking methods, which take several days to complete a batch of licorice-type candy, have been replaced by continuous cooking methods for high-throughput, economic and convenient processing.

Licorice manufacturers can manipulate any or all of these parameters to control the textural properties of their licorice product.

To achieve the desired final moisture content of about 15% in licorice and fruit-twist products yet still have sufficient water during cooking to obtain the desired extent of starch gelatinization, cooking conditions must be carefully controlled. As noted in Section 14.4.2.1, sugar raises the temperature necessary for starch gelatinization by depleting the water molecules available for hydration of the starch granule. Sugar content also affects the boiling point temperature (see Section 2.7), making the interplay between the starch gelatinization and boiling point elevation curves a critical control element for licorice-type candies.

Figure 12.8 compares the approximate starch gelatinization and boiling point elevation curves for atmospheric cooking of licorice candy (Knoch 1976). Due to the variable influences of sugar phase composition (average molecular weight) and starch type, these curves can only be taken as guidelines. Despite this limitation, Figure 12.8 can be used to understand starch gelatinization during open batch cooking of licorice formulations. The dashed line in Figure 12.8 represents the onset temperature for starch gelatinization in a licorice formulation of corresponding concentration (total concentration includes sugars and protein). As the sugar content increases (and water content decreases), the temperature needed for onset of starch gelatinization increases. Another way to interpret this curve is that temperatures lower than the dashed line for a given

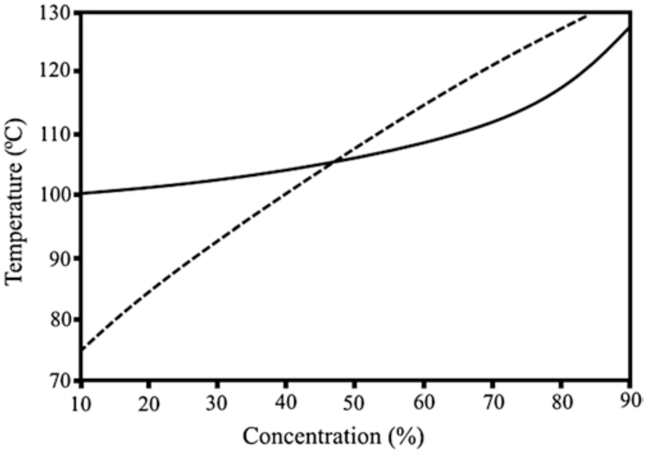


Figure 12.8 Approximate temperatures for starch gelatinization and boiling point elevation of licorice. *Dashed line* represents approximate temperature necessary for starch gelatinization in licorice formulation of certain concentration (sugars and proteins). *Solid line* represents approximate boiling point elevation curve for licorice formulation (Adapted from Knoch 1976)

sugar concentration in licorice do not cause gelatinization, whereas temperatures above the dotted line lead to starch gelatinization. However, atmospheric cooking of the sugar/flour mixture for licorice follows a boiling point elevation curve, as shown approximately by the solid line in Figure 12.8. Thus, if a licorice formulation is cooked in an open vessel at atmospheric pressure, gelatinization ceases once the boiling temperature crosses the gelatinization temperature line. At this point, the concentrated sugars protect the starch from undergoing further gelatinization. The result is a product with insufficient gelatinization– the licorice is firm but with a bread-like consistency. According to the conditions shown in Figure 12.8, the point where gelatinization stops occurs at a temperature of about 107–108 °C (224–226 °F).

In traditional batch licorice cooking processes, the candy maker would sometimes hold back a portion of the liquid sugars until the later stages of cooking. The proper degree of gelatinization would be accomplished during cooking of the dilute sugar solution, after which the rest of the sugar would be added to the batch to cook off water. Further starch gelatinization was prevented due to the higher concentration of sugars.

Continuous processing units use high pressure cooking systems (scraped surface heat exchangers or twin screw extruders), which increase the boiling point temperatures at all sugar concentrations (see Section 2.7) and enhance gelatinization. By increasing boiling temperatures (shifting the solid line in Figure 12.8 to higher temperatures), gelatinization can occur throughout the cooking process. For this reason, continuous licorice processing operations tend to slightly overgelatinize the starch, leading to a more rubbery licorice texture. In fact, the difference in texture between open-kettle cooked or continuous cooked licorice is quite significant, with traditional licorice having a significantly shorter texture than continuously processed licorice (Clark 1996).

12.4.1.5 Mixed Hydrocolloids

In Table 12.1, the physical attributes of candies made with different hydrocolloids were summarized. However, a wide range of products are available on the market that employ mixtures of different stabilizers to give confections with textures intermediate to the separate stabilizers. The science behind hydrocolloid mixing behavior is complex and the ability to predict the textural properties of a mixture is still quite limited despite application of synthetic polymer blending laws to mixed confectionery gels (Habeych et al. 2009; BeMiller 2011).

In general, mixtures of two hydrocolloids give a product with a texture somewhere between the two individual molecules, although this is not always the case. For example, addition of about 0.5% HM pectin to gelatin gives a shorter and firmer texture than gelatin alone. Addition of less than 0.3% HM pectin to gelatin also increases the melting point of gelatin. Also, starch added to pectin gives a gel that is less sticky than pectin alone, whereas pectin added to a starch gel shortens the texture. When gelatin is added to modified starch, the resulting candy has a chewier texture than the starch jelly itself. The combinations of two or more hydrocolloids to produce new and unique textures are almost endless.

The behavior of two hydrocolloids mixed in an aqueous sugar solution can be extremely complex, depending on both how (or if) the two different molecules interact and how the system is processed (cooling rates, shear, etc.). These interactions determine whether a single mixed phase is formed or whether multiple distinct phases form, which, of course, determines the physical attributes (appearance, rheological properties, etc.) of the mixture. Further, most hydrocolloid mixtures are inherently unstable, with each of the individual hydrocolloids preferring to separate from the mixture into its own phase (de Mars and Ziegler 2001). This phase separation, or demixing of a hydrocolloid gel, may occur over time, leading to the end of shelf life due to changes in appearance, texture, moisture separation, and flavor release. Phase separation over time, a thermodynamically driven process, may be due to differences in hydrophobicity between hydrocolloids, dissimilarity in shape or structure, and the rigidity (or flexibility) of branched chain structures.

The combination of hydrocolloids may affect the setting or gelation properties over and above the effects on texture. Process conditions may need to be modified to ensure adequate time for gelation to occur. For example, it is widely known that hydrocolloids significantly affect the pasting and gelatinization of starch (BeMiller 2011), potentially causing issues with processing.

Recent attempts to fortify gummy and jelly candies with proteins have met with similar effects based on mixing hydrocolloids, where the protein can significantly influence texture, sensory and shelf life. For example, Siegwein et al. (2011) added soy protein isolate to starch gummy candies and found that textural properties (hardness, gumminess, cohesiveness) were significantly influenced by the addition of the protein. Changes over storage were also different based on the addition of protein, with the protein enhanced confection firming much more dramatically than the control.

Although mixtures of stabilizers can potentially provide uniquely textured candies, the science that underlies the phase behavior of mixed hydrocolloids must be better understood to truly take advantage of the wide range of new confectionery products that become available. In particular, the stability of these mixtures to phase separation during storage must be better understood to produce high quality confections with maximal shelf life.

12.4.2 Flavor Release

The ability of flavor molecules to release into the mouth during consumption is dependent on numerous complex processes and interactions, both thermodynamic and kinetic in nature. Flavor molecules, which vary in hydrophilicity, partition according to thermodynamic laws between the three phase system in the mouth, namely the candy matrix, saliva and air, during consumption. The rate at which partitioning occurs depends on the principles of mass transport during consumption. The textural properties of the gel system play an important role in determining mass transport properties whereas the interactions between hydrocolloid matrix and the flavor molecule determine the partition behavior (Boland et al. 2004).

As noted in Table 12.1, different hydrocolloids exhibit both different textural attributes as well as flavor release. Pectin, with a short and tender bite, is seen to exhibit the most rapid flavor release whereas gelatin, with a firm, elastic texture, exhibits the slowest flavor release. The moderate chewiness of the starch gel gives flavor release intermediate to that of pectin and gelatin gels. Not surprisingly, the easier the gel structure breaks apart in the mouth, the faster the flavor release. This behavior arises from the effects of mass transport on flavor perception, where transport of the flavor from gel to saliva and air is enhanced by the ease of exposing the gel interior to the mouth.

Beyond textural effects, though, each hydrocolloid interacts in a unique way with the flavor molecules in the gummy or jelly candy. Boland et al. (2004), for example, found that in general, starch gels preferentially retained hydrophilic flavor compounds whereas pectin gels preferentially retained hydrophobic flavor compounds (relative to partitioning of flavors to air). This was related to the formation of the gel structure itself, with hydrophobic components of pectin being responsible for capturing the hydrophobic flavor molecules. No evidence for preferential flavor binding to gelatin was found.

Saliva also plays an important role in distinguishing flavor release, in part by enhancing mass transport from gel to the mouth. However, saliva also contains compounds (mucin and α-amylase) that influence flavor release. Mucin, for example, can bind with hydrophobic components, thereby decreasing their rate of release into oral cavity. In confections, the sugars also compete for these mucin binding sites and can influence flavor release. In starch jelly candies, the α-amylase in the mouth causes degradation of the starch almost immediately, which can help with flavor release.

12.4.3 Shelf Life

The shelf life of hydrocolloid-based candies (gummies, jellies, licorice and fruit twists, etc.) is primarily related to moisture migration causing the candy to either get too hard (moisture loss) or become sticky (moisture uptake). Both finishing method (oiling, sanding, etc.) and choice of packaging materials affect shelf life through an effect on moisture migration. Other potential changes that can occur during storage include changes to the hydrocolloid (e.g., retrogradation) and changes to colors and flavors.

Due to the relatively high moisture content (up to 20%), water activity (see Section 3.4) of most gummy and jelly candies is relatively high. Water activity values in the range of 0.5–0.75 are common (see Table 3.1). Since average relative humidity is often less than the equilibrium relative humidity of these candies, the most common problem during storage is moisture loss. Drying out of hydrocolloid-based candies leads to increased hardness, eventually reaching the point where the consumer no longer finds the texture acceptable. In extreme cases, for example when an open bag of licorice/fruit twists is left out in a dry environment (winter in northern climates or desert areas), the candy can become so brittle within a few weeks that it shatters when struck against a hard object. In this case, the decrease in water content causes the glass transition temperature of the candy matrix to approach room temperature, resulting in a hard, brittle texture.

Sanding and oiling can impede moisture loss but their effects are small when the candy is exposed to extreme conditions. Addition of a small amount of humectant (glycerol, sorbitol, etc.) can help maintain plasticity during storage. In fact, sugar-free candies tend to have longer shelf life because of the humectant nature of the ingredients. Packaging materials with a good moisture barrier that is properly sealed can reduce moisture loss and extend shelf life. In most cases, however, once the package has been opened and the candy is then exposed to external conditions, hardening occurs rapidly. Very few gummy and jelly candies are double-wrapped to protect uneaten candies from losing moisture once the overwrap package has been opened. The use of resealable packages can also potentially extend shelf life, but the costs of such packaging are seldom economically viable.

Gummies, jellies and licorices, with their higher moisture content, should be stored with a relative humidity (RH) of 55–65%. This will reduce the tendency for drying to occur. When storage temperatures are reduced from the standard 20 °C (68 °F), shelf life is increased. A general rule is that every 10 °C (18 °F) will double shelf life.

In addition to moisture loss, volatile flavors can diffuse out of the candy into the surrounding air. For this reason, packaging material should have a good oxygen barrier and be sealed properly to maintain flavor levels. Exposure to light with clear packaging may affect sensitive colors and flavors that will lead to unacceptable appearance and/or flavors. Storage conditions that have off-odors and inconsistent temperatures can also affect finished product shelf life.

12.5 Troubleshooting

A wide range of potential problems can arise with gummy and jelly candies, due either to formulation issues, processing problems or storage conditions.

12.5.1 Gummies and Jellies

Gummies and jellies come in a wide range of textures, from soft and easy to bite to hard and tough to chew. Primarily, hardness of this type of candy is related to the nature of the hydrocolloid and the water content. Typically, higher hydrocolloid content and lower water content lead to firmer candies. If the candy is too soft, water content could be too high, hydrocolloid concentration too low, or the hydrocolloid selection was incorrect (e.g., bloom strength too low for gelatin). Factors that could lead to water content being too high include cook temperature, sweetener mixture (including potential sucrose inversion), and holding for too short a time in drying starch. If texture is too tough, water content may be too low or the hydrocolloid concentration is too high. Often, hardening of gummies and jellies over time is due to moisture loss through the packaging. Also, the Maillard reaction between gelatin and sugars can occur slowly over time, also leading to hardening of gummy candies.

If for some reason, the candy does not set or is too weak, there are a number of potential causes, besides reduced water content, depending on the type of candy. In HM pectin jellies, lack of setting may be due to improper pH. Check the acid addition step to ensure that pH is lowered adequately to allow the pectin to gel. Alternatively, the pectin candy mass may pre-gel in the depositor, leading to a weak, incoherent candy. Gummy candies that do not set may be due to excessive degradation of the gelatin molecule, preventing it from forming a strong network. Excessive acid addition or holding an acidified sugar syrup containing gelatin for too long at elevated temperatures may also lead to degradation and weak texture. For starch jellies, use of improper starch to match the cooking conditions (high amylose starch in open kettle cooking) or providing insufficient water for starch gelatinization will also lead to soft or even runny candies.

Gummy and jelly candies have the potential to grain over time, particularly at the surface of the candy. Usually, graining is related to improper sucrose to glucose syrup ratio and/or improper viscosity. As discussed in Section 2.10, graining occurs if supersaturation is sufficiently high and kinetic constraints are insufficient to prevent crystal formation. Not surprisingly, the key to preventing graining is to reduce the sucrose content and increase the concentration of other sugars that act as doctoring agents such as glucose or invert sugar. Graining can also appear if all sucrose crystals were never initially dissolved during the cooking process or processing abuse (such as improper pumping or scraping) will cause crystal formation.

Gelatin gummies that deform and lose their shape is most likely due to the thermo-reversibility of the gelatin gel. If temperature is too high, for example, during holding prior to oiling, the gelatin gel will melt, turning the candy into a fluid mass that quickly flows and loses its shape. Holding temperatures of gelatin gummies must be well below the melting point of gelatin to prevent deformation. Usually, temperatures less than about 30 °C (86 °F) provide safe storage of gummy candies. Gelatin-based candies should not be shipped during warm seasons without cooling to prevent melting. The candy will re-solidify again when cooled, but will not longer have the original shape.

Gummy and jelly candies can sometimes be sticky and/or sweat. This defect may be due to excess reducing sugar or inversion of the sucrose, although formulation with high DE glucose syrup may also cause sticky candies as the low molecular weight sugars are hygroscopic and easily pick up moisture from the environment. Improper pH or holding the sugar syrup at high temperatures for long times also can lead to excessive inversion. Use of natural fruit juices or pulps with variable pH may also lead to problems with moisture pick up. Syneresis, exudation of moisture to the surface from within the gel, may occur if the gel is weak, broken or damaged in any way. Improper or insufficient gelation can lead to syneresis. In mixed gel systems, phase separation can occur between the two hydrocolloids, which can cause release of the syrup phase to the surface.

Typically, microbial growth is not an issue in gummy or jelly candies because of the reduced water activity. If sweating at the surface or significant moisture uptake occurs, however, mold growth at the surface may occur.

With proteins as gelling agents, foaming and air entrainment can cause problems in appearance of gummy candies. When proteins are added to the batch after cooking the sugar syrup, care must be taken to prevent air incorporation. Even excessive mixing when minor ingredients are added can lead to foam formation in gelatin candy syrups. A de-aeration step, often accomplished by pulling a vacuum on the syrup, may be necessary to ensure that no air is entrained in the candy mass.

12.5.2 Flour-Based Candy (Licorice and Fruit Twists)

The primary problems with licorice and fruit twist candies relate to undesired textures of the finished candy, which ultimately are due either to the extent of starch gelatinization, improper final water content or too high a concentration of small molecular weight sugars. If the candy is tough, with a chewy elastic texture, it is likely that the starch has been over-gelatinized. This may occur for a number of reasons, including (1) the slurry was overcooked, (2) the flour used was not satisfactory, (3) sugar content was too low at the start of cooking, and (4) water content was too high in the slurry. Each of these factors could cause excessive pasting of the starch, not leaving enough intact starch granules. On the other side, if the candy is too short or soft, it is most likely due to starch that has been under-gelatinized. This may occur because (1) the slurry was undercooked, (2) there was insufficient water in the slurry, or (3) sugar content was too high at the start of cooking.

Candy that is too hard or too soft may be due to improper final water content. Low water content, as might happen if the candy is allowed to dry too much in stoving or is left open to dry air, causes a substantial increase in hardness. Alternatively, high water content may cause the candy to be too soft, but also might lead to potential mold problems if water activity is too high. Water activity should never be higher than 0.65–0.68 unless a yeast and mold inhibitor is added to the formulation. Candy that is sticky may also be related to high water content, but this also may be due to excessive levels of low molecular weight sugars (invert sugar) or the lack of fat and/or emulsifier.

12.5.3 Problems with the Starch Mogul

Certain types of problems with gummy and jelly candies may be due to improper starch mogul operations. These problems generally relate to the characteristics of the starch used in the mogul. If the candy shape does not come out as desired, it is possible that the starch boards are not printing properly so the depression does not take on the desired shape. From the starch side, this can happen if the starch is too hot/cold/wet/dry. Even high relative humidity in the depositing room can cause sufficient moisture uptake from the air to the starch that a good impression cannot be made. Improper shapes can also be caused by a dirty mold board, where the actual shape is not being impressed into the starch.

A white starchy crust or blemish on the surface of the candy piece indicates that the molding starch had gotten wet, most likely because water was allowed to drip onto the starch. Steam line connections should be checked and sealed if faulty, and water used for lubrication should not spray onto the starch. Another potential problem particularly in gelatin gummies deposited into molding starch is an excessive starch skin on the candy surface. The problem is most likely due to high moisture content (>7.5%) in the molding starch, but it may also be due to low depositing solids (<70%) or high depositing temperature (>93 °C; 200 °F).

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13 Sugar and Sugar-Free Panned Confections

13.1 Introduction

Sugar-panned candies may be broadly defined as candies where a sugar shell has been applied to a center (sometimes called comfit or dragees) through sequential addition of syrup as the piece is tumbling in a revolving pan. Sugar shells may have either a hard, brittle texture (hard panning) or a soft, easily broken texture (soft panning), with the shell characteristics related to the syrup composition and the nature of sugar crystallization as the shell material is applied. Although the term sugar is often used here, sugar-free components are also panned as well. Specific details related to sugar-free applications are noted as pertinent. A third type of panning involves application of a chocolate coating; chocolate panning is covered in Chapter 17. Preparation of centers is generally described in the chapters related to that particular candy category (e.g., jelly candies for jelly bean centers).

Sugar panning reputedly has its origins in seventeenth century France, when nut pieces were coated in sugar by rolling them in a pan of molten sugar, although there is evidence that seeds or thin strips of cinnamon were coated in sugar in a process similar to panning well before the seventeenth century. The nuts (or seeds, etc.) were rolled back and forth through the hot sugar syrup as the pan, suspended over a fire for heating, was manually tilted back and forth. A crystallized sugar shell slowly built up as the water evaporated from the syrup layer. Development of the rotating pan allowed better control of tumbling of the centers and enhanced the panning process by allowing one operator to control multiple pans. More recently, many panning operations have been automated on a large scale, with syrup addition and air handling being computer controlled.

Sugar panned candies may be distinguished by the nature of the sugar shell that is applied to the center, with the main distinction between hard and soft-panned candies being the texture of the sugar shell. In soft panning, the relatively larger crystals that make up the sugar shell, as shown schematically in Figure 13.1, provide little resistance to breakage during consumption. The shell fractures easily, with little force needed. Examples of soft-panned candies are jelly beans and fruit sours. In hard panning, the shell is highly crystalline with many small crystals fused together, as shown schematically in Figure 13.2. Thus, it takes on a hard, brittle character and requires relatively more force applied by the teeth to break through the shell. This hard, brittle shell often provides a textural contrast with the candy piece inside (e.g., chocolate). This hard sugar shell is one way to prevent chocolate from melting in your hand. Examples of hard panned candies are sugar-coated chocolate lentils, nuts (e.g., Jordan almonds), licorice bits, and gum balls. Some panned candies have mixed sugar shells, with a soft-panned layer(s) applied first, prior to finishing with hard-panned sugar shells. With limited exceptions, mixing soft and hard-panned shells is typically a convenient way to

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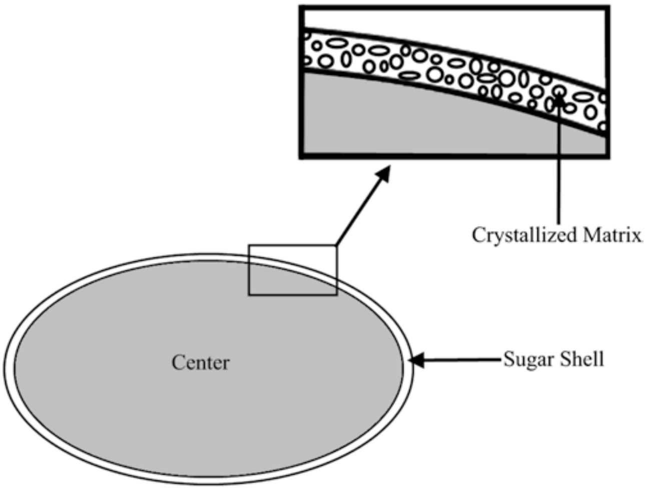


Figure 13.1 Schematic cross section of soft panned sugar shell

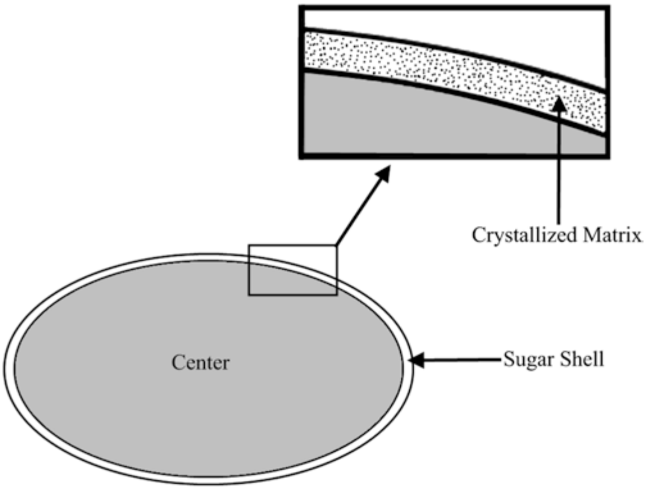


Figure 13.2 Schematic cross section of a hard-panned sugar shell

speed the hard panning process. However, the risk is that the hard, brittle texture desired in a hard-panned candy may be compromised with too much of a soft-shell; thus, this approach of speeding the hard panning process must be used with caution.

Another way to distinguish between soft and hard panning is from a crystallization standpoint. Hard panning refers to the process of creating a thin layer of crystallizing syrup and allowing that syrup to crystallize. Soft panning is often considered to be noncrystallizing, where the engrossing syrup is simply the glue that holds the sugar particles added to complete the coating layer.

To make panned candies, sequential layers of sugar syrup are applied to the centers as they tumble in a revolving pan or drum. In hard panning, a supersaturated sugar syrup is applied to the center and allowed to crystallize as it dries in the pan, leaving a hard and brittle layer composed of numerous small crystals. Sequential syrup applications followed by a drying period allow the shell to build up to the desired thickness. Depending on the desired shell thickness, 30 or more sequential applications may be needed to build the shell. In soft panning, a noncrystallizing sugar syrup is applied to the center followed by addition of sugar powders. The shell is built up by packing dry powders into the noncrystallizing syrup to make a firm coating. The sequential application of sugar syrup and powdered sugar to the center is continued until the shell has reached the intended weight or thickness for the desired candy piece. Usually, four to ten sequential applications are sufficient to build the desired shell thickness.

After the shell has completely solidified and moisture has equilibrated between the shell and the center, the panned candy is polished and glazed to give an attractive, shiny appearance. For soft-panned candies, there is usually a smoothing step, with low solids concentration, to dissolve any sugar powders prior to polishing. To apply the polish, the pieces are tumbled, generally in the same pan, as polishes and waxes are added. The polish material is allowed to dry or solidify while tumbling to give a shiny appearance and to protect the shell from environmental conditions.

The sugar shell and polish/glaze layer provide some protection from external conditions, giving panned goods an exceptionally long shelf life. A hard panned candy, in particular, may have shelf life well over a year, with little change in product quality if stored in good conditions. However, changes in the center characteristics may still take place over time, particularly in soft-panned candies where water migration takes place, albeit at a reduced rate. Hardening of jelly centers over time due to moisture loss through the sugar shell remains the primary cause for the end of shelf life for soft-panned candies, although the rate of hardening is much reduced by the sugar shell (as compared to the jelly candy by itself, without the shell).

13.2 Formulations and Ingredients

Panned candies encompass a very wide range of confections; however, the common theme is that they are coated with either a soft or hard sugar shell. This coating gives a distinct texture to these candies and makes them uniquely different from any other candy. Typically, a panned candy center, whether soft or hard panned, is coated with three distinct layers (see Figure 13.3). First, a pre-coating layer is applied to the center to help ensure good adhesion of the sugar shell. This is particularly important when the center contains fats since a sugar shell applied directly to something like nuts or chocolate centers does not readily adhere. The second layer is the sugar shell itself, which is usually the largest/thickest of the three layers. The final layer applied to the surface of the sugar shell is the polish/glaze layer.

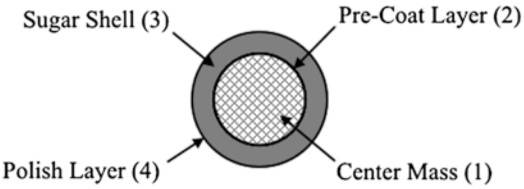


Figure 13.3 General layers found in sugar-panned candies

Table 13.1 Examples of centers used for panned candies

Hard	Soft
Chocolate	Jelly beans/eggs
Nuts	Jelly fruit sours
Grains of sugar	Jelly rods
Gum (balls or dragees)	Caramels
Licorice	Cinnamon centers
Compressed tablet	Baked bean candies
	Marshmallow eggs

13.2.1 Centers

Almost any type of center can be used for panning as long as it can be adequately tumbled in a revolving pan. Table 13.1 gives numerous examples of types of centers that have been used in soft and hard sugar panning, although this list is by no means complete. The list of centers that have been (or can be) panned is quite extensive although not all panned centers are marketed commercially.

To be a candidate for panning, a center must have certain qualities. The center must neither be too heavy nor too light. Either extreme inhibits tumbling ability in the revolving pan and impedes coating of the piece with the sugar shell. It is the force applied during tumbling that provides proper coating; if those forces are too high or too low, problems arise during application of the sugar shell. Size and density of the center are critical to getting a good, uniform coating – it is desirable to have centers that are all the same size and weight (density) so that no segregation occurs during tumbling. Also, the center must be sufficiently robust to stand up to the forces of tumbling without breaking apart or causing excessive dust. This is particularly true in large capacity pans/drums where the tumbling forces can be quite substantial. Brittle centers with sharp edges, for example, are very difficult to pan.

The shape of the center also affects its ability to be sugar coated. Spherical shapes are the easiest to work with since the tumbling forces are applied uniformly over the entire surface, tending to uniformly smooth out the sugar shell. Centers with sharp corners are particularly difficult to coat since the sugar syrup does not build up at the edge. Uneven or ridged centers may result in an unsightly shell. Also, centers with flat surfaces are difficult to pan without sticking together. The large surfaces wetted by the sugar syrup tend to stick together and are nearly impossible to break apart with the tumbling action.

13.2.2 Pre-coat Material

To ensure that the sugar shell adheres uniformly to the center, it is sometimes necessary to apply a pre-coating layer on the center. For example, the lipid surface of a nut or chocolate lentil does not provide good adhesion for aqueous-based sugar syrup. Thus, nuts and chocolate centers are typically pre-coated with a material that serves to bridge the oil and water phases prior to sugar panning to make sure that the sugar shells remains attached to the center. The pre-coat also acts as an oil barrier in this case. The pre-coat layer may also act as a water barrier in cases where water from the engrossing syrup may damage the center (i.e., certain tablets and gums).

Besides enhancing adhesion of the sugar shell and serving as a water barrier, pre-coating also serves to fill in depressions or rough spots in centers to make a smoother surface. It can also enhance the strength of easily deformed centers by providing a more rigid structure. Finally, a pre-coating layer can help improve flexibility of the center by acting as a sort of "shock absorber", thereby minimizing chipping and cracking of a hard sugar shell.

The nature of the pre-coat material depends on the type of center and shell being applied. Jelly centers for soft panning are typically sanded with fine sugar crystals to help adhesion of the engrossing syrup (as well as to prevent the centers from sticking together prior to panning). Coating of centers for sugar-panned candies generally means application of a thin layer of gum (e.g., gum arabic), protein (e.g., gelatin), or long-chain carbohydrates (i.e., dextrin, low DE maltodextrin or modified starches). Aqueous preparations of these materials can be applied directly to the center in the initial stage of panning and allow adhesion of the sugar shell during the subsequent build-up of the shell. These layers may be dried by addition of starch or powdered sugar. Flavor and acid may sometimes be added at this point as well.

13.2.3 Sugar Shell

The nature of the shell material applied during panning is quite different for hard and soft sugar panning. In hard panning, sugar crystals nucleate directly from the supersaturated sugar syrup as each layer is allowed to dry or seeded from the sugar crystal dust that forms as the previous layer dries. Thus, crystallizing sugars are used in the engrossing syrups for hard panning. In soft panning, the sugar syrup acts simply as a glue to hold the sugar crystals added during the dry charge steps, without substantial crystallization.

13.2.3.1 Soft Panning

In soft panning, the sugar syrup acts essentially as a binder to hold together the crystal powder added during the dry charge stages. As such, the engrossing syrup applied to the centers in soft panning is often considered to be noncrystallizing, although in reality a small amount of sugar may crystallize from the solution particularly as temperature or moisture content changes during shell application and curing.

Typically, engrossing syrup for soft panning is a mixture of sucrose and glucose syrup, often at a ratio of about 1:1, on a solids basis, to minimize sucrose crystallization. Either 43 or 63 DE glucose syrup can be used although shell texture will be slightly softer with higher DE. A slightly higher ratio of sucrose to glucose syrup leads to a slightly harder sugar shell since some of the sugar in the syrup crystallizes onto the dry powder charge and leads to bridging of crystals in the shell. Engrossing syrup can be made entirely from glucose syrup with no risk of sucrose crystallization, giving a very soft texture; however, glucose syrup typically needs to be diluted with water (to as low as 65% solids content) to reduce viscosity to a suitable value for application. Specialty syrups with higher levels of dextrose or maltose may also be used. Engrossing syrup concentration is typically between 70% and 78%, with higher concentrations preferred as long as the viscosity of the syrup is appropriate for good coverage. Temperature of application generally falls between 35 and 71 °C (95 and 160 °F), depending on the heat sensitivity of the center and the engrossing syrup viscosity. Higher temperature application generally leads to firmer or crunchier shells as more sugar crystallizes from solution when the syrup cools to room temperature after completion of panning.

The dry powder charge added after each syrup addition may be either fine granulated sugar, Baker's special confectioner's sugar or powdered sugar, with addition typically in decreasing order of particle size. Larger particulate powders (extra fine granular, etc.) are added in the early stages to help build up the shell more quickly. Finer powders (6× and 10× confectioner's sugar) are added last to ensure the smoothest product finish.

Soft sugar shells may be made from dextrose or from sugar-free materials, although the availability of fine-powdered polyols may limit the sweetener choice. Generally, the same principles apply to process dextrose or sugar-free shells: the engrossing syrup should be mostly noncrystallizing and the powder charge should be as fine as possible. For dextrose panning, the engrossing syrup is often comprised of either high fructose or high maltose glucose syrup to minimize excess dextrose crystallization upon addition of the powder charge. Sugar-free, soft panned candies are often made from maltitol syrups packed with either crystalline sorbitol, xylitol or isomalt powders. Addition of a high intensity sweetener to the engrossing syrup may be required for sugar-free coatings. More information regarding soft panning with sugar alcohols can be found in Boutin (1992).

13.2.3.2 Hard Panning

Hard panned shells most often consist of crystalline sucrose, dextrose or sugar alcohols (i.e., sorbitol, xylitol, isomalt, maltitol, etc.). The key factors for the sugar syrup are the viscosity and supersaturation of the syrup as it is applied to the center, as well as the crystallization rate of the sugar. Viscosity of the engrossing syrup should be less than about 200 cP to ensure proper coating. However, too low an engrossing syrup viscosity usually means elevated water content, which is undesirable since longer cycle times are required to remove that excess water and problems with controlling crystallization may arise.

Due to the cyclic nature of hard panning (sequential syrup application followed by drying and crystallization), the syrup must crystallize quickly after application. Primarily, this means that it must have a high supersaturation and high purity. The solubility of the sugar must be appropriate so that it is sufficiently supersaturated (see Sections 2.8 and 2.10) at the conditions of application in the pan without crystallizing prior to application. Note that sucrose-based engrossing syrups should be completely free of crystals. The presence of sucrose crystals in the syrup during panning causes the sugar shell to be uneven. Interestingly, in dextrose-based panning, seed crystals present in the engrossing syrup do not cause problems with shell appearance.

Proper choice of temperature and concentration of the engrossing syrup is required. For sucrose syrups, concentrations of 67–72% are often used, depending on application temperature, which may vary between 18 and 66 °C (65 and 150 °F). For heat-sensitive centers (e.g., chocolate), lower temperatures, 18–27 °C (65–80 °F), are needed to prevent melting. Deformation of gum and chew/taffy centers may occur if application temperatures are above about 38 °C (100 °F). Centers that are not heat sensitive (e.g., jawbreakers) can be panned at temperatures of up about 66 °C (150 °F).

Since sucrose solubility at room temperature is only 67% (Section 2.8), lower engrossing temperatures require lower concentrations to prevent premature crystallization (and to control viscosity). Higher concentrations (75–77%) can be used with hotter syrup application temperatures, as long as sucrose inversion does not occur. Towards the end of shell build-up, when developing a smooth shell is most critical, even lower syrup concentrations are often used. The solids concentration of smoothing syrups is usually less than 67% and perhaps even as low as 55–60% for the final applications to ensure a smooth surface. Smoothing syrups are also added close to room temperature to prevent dissolution and recrystallization of previous layers.

Furthermore, the presence of any impurities, like glucose syrup in a sucrose solution or mannitol in a sorbitol solution, retard crystallization and slow down the panning process. Even excessive inversion of sucrose due to long hold times, low pH or high hold temperatures can slow panning cycles. Thus, the engrossing syrup for hard panning typically has minimal impurities or doctoring agents so as not to inhibit crystallization. Having said that, pan operators sometimes add low levels of certain ingredients to moderate the properties of the sugar shell in hard panning. For example, 1% or 2% dextrose syrup or 0.5–1% gum arabic may be used to make a slightly more pliable hard sugar shell, which may be useful for preventing cracking or coating a center with a sharp edge.

Dextrose and polyol hard panning generally follow the same principles as sucrose panning, although some differences are noted based on the differences in solubility, viscosity and crystallization propensity of each sweetener. Dextrose hard panning has been practiced for several decades with little problem. In fact, in some ways, dextrose hard panning is easier than sucrose hard panning because of the higher solubility of dextrose at elevated temperatures and the lower viscosity of glucose syrups. Higher concentration engrossing syrups can be used in dextrose panning while still retaining the desired syrup viscosity. Crystallization of dextrose under these conditions is sufficiently rapid to promote a hard sugar shell. The dextrose shell is less brittle than the sucrose shell, primarily because of the difference in crystalline network structure.

Various polyols can be used for hard panning, including xylitol, sorbitol and isomalt. However, conditions of use for each polyol change slightly depending on solubility concentration and viscosity. Newer technologies use suspensions to accelerate/facilitate faster crystallization. Boutin (1992) also discusses hard panning with various polyols.

13.2.4 Colors

Either the soluble or lake forms of colors may be used in sugar-panned candy shells. Dyes tend to give brighter colors than lakes but are more likely to bleed, especially if moisture content of the shell is not completely equilibrated. The advantage of using lakes is that any moisture migration within the shell will be less likely to cause color changes (e.g., mottled appearance) than when dyes are used. Lakes also provide more hiding power since they are opaque. In some sugar-panned products, particularly hard-panned candies, titanium dioxide is used in early layers of the shell to provide a richer color. While titanium dioxide helps to provide an excellent finished color, it has become less popular with consumers. There are now compounds based on starches and other materials that can be used as a replacement for titanium dioxide. In hot panning processes, a heat sensitive color must be chosen to prevent fading.

“Natural” (exempt from certification) colors have seen increasing use in recent years. They are available in a variety of forms. Their usage rate, vibrancy and sensitivity to pH may be different than FD & C dyes and lakes. They are frequently heat sensitive and often possess distinct flavors (e.g., red beet). Most exempt colors are dyes and thus, are prone to moisture migration. The addition of rice flour to the color has proven successful and beneficial in improving color intensity and opacity. The exempt from certification colors are generally made from the following materials:

Reds: carmine, iron oxide, anthocyanins;
Oranges: β-carotene, paprika;
Yellows: turmeric, riboflavin, β−carotene;
Blues: anthocyanins, spirulina;
Greens: mixtures of blues and yellows;
Violets: anthocyanins, carmine, mixture of blues and reds;
Blacks: vegetable carbon, iron oxide, caramel;
Whites: titanium dioxide, opacifying agents.

Colors are generally added throughout the soft panning process, but typically only constitute the last 5–15 coats for hard panned candies. Prior to addition of the color layer in hard panning, the surface should be completely smooth. An uneven shell surface will result in uneven thickness of the color layer and thus, an uneven appearance.

13.2.5 Flavors

Flavors are occasionally used in hard-panned shells and are typically added in the shell of soft-panned candies, particularly in products like jelly beans. Sometimes the carrier used to deliver flavors may cause problems in the panning process. For example, the propylene glycol present in certain flavors may hold moisture (as a humectant) in the shell of a soft-panned candy, which can lead to stickiness during storage. Oil-based flavors can be difficult to use in sugar panning because they lubricate the pan, causing the centers to slide instead of tumble, and may separate from the aqueous sugar shell, causing a mottled appearance. With care, however, low levels of oil-based flavors (e.g., mints, certain citrus flavors, etc.) can be used without problems.

13.2.6 Acids

Organic acids (lactic, citric, malic, etc.) can be used in sugar-panned candies to provide tartness. However, problems may arise in sucrose-based shells due to excessive sucrose inversion if liquid acids are added to the engrossing syrup. In hard-panned candies, invert sugar would inhibit crystallization and lead to a softer shell texture. In soft-panned candies, excess invert sugar in the engrossing syrup can cause collapse of the shell, enhance mottling when water-soluble colors are used, and cause glazes to appear dull.

There are several approaches that can be used to prevent problems of inversion due to acid addition to the engrossing syrup. For one, adding the acid to the engrossing syrup at the last possible moment means there will be less time for inversion to occur. Also, using a buffered acid system may moderate the effects of the acid on sucrose inversion. Powdered acids, whether encapsulated or not, can be applied to the center before panning to provide a sour taste without affecting the engrossing operation. Finally, using acid with a sweetener other than sucrose may be a possibility. Dextrose and polyols are not influenced by acids and thus, will not exhibit the same negative effects.

13.2.7 Polish and Glaze

Panned candies are generally polished and glazed to provide a shiny appearance and to protect the piece from subsequent abuse. Although sometimes the terms polish and glaze are used interchangeably (and together), they serve different purposes. A polish provides a glossy surface to a panned confection, whereas a glaze is a sealant that retains the gloss of the polish with a stable film. Since the use of polishes and glazes is often combined, some choose to simply use the term finishing agents to describe polishing and sealing the surface of panned goods. See Section 6.5 for more details.

Numerous finishing agents have been used for panned goods, as listed in Table 13.2. These can be generally categorized as waxes, gums, starches, carbohydrates, proteins or shellacs (confectioners glaze). Although usually applied in liquid form, waxes can also be applied in solid or powdered form. Depending on the nature of the finishing

Table 13.2 Classes of polishing and glazing agents

Solid	Type	Examples	
	Wax	Carnauba, beeswax, candelilla, paraffin, microcrystalline wax	
Liquid	**Type**	**Solvent**	**Examples**
	Gum	Water	Gum arabic, xanthan gum
	Starch	Water	Maltodextrin, starch (wheat, rice, corn, potato, etc.)
	Carbohydrate	Water	Corn syrup, sucrose, pectin
	Wax	Alcohol, vegetable oil, mineral oil	Carnauba, beeswax, etc.
	Shellac	Alcohol	
	Protein	Alcohol	Zein (corn protein)

agent, it may be solubilized in water, alcohol or some other solvent (limonene, acetone, mineral oil, vegetable oil, etc.). The choice of solvent is becoming more important as manufacturing facilities must concern themselves with emissions of volatile organic compounds (VOCs).

13.3 Processing

Sugar panning has traditionally been done in revolving batch pans. However, numerous advances in coating technology have changed the nature of the panning room in many confectionery plants. Although it is not uncommon to still see banks of revolving pans, other technologies, like the belt coater and large automated drums, are becoming more and more common in the candy industry. The efficiency, higher production capacity, and automation of these new panning technologies make them an attractive alternative. Newer technologies, such as film coaters from the pharmaceutical industry, are gaining in popularity and have the potential to change the confectionery panning industry.

However, some processes resist automation, requiring careful attention by an experienced operator to ensure a high-quality, consistent product. Perhaps the reason that panning has often been considered more of an art than a science is due to the large number of parameters that influence the panning process. From the engrossing syrup to the polishing procedure, numerous operating parameters and formulation variables can have a significant impact on the quality of sugar-panned goods. Table 13.3 summarizes the various parameters that can impact panning.

13.3.1 Sugar Shell Application

Numerous different types of rotating pans or drums can be used to sugar-pan confections. Although the traditional tulip-shaped pan is still probably the most commonly used, improved and more efficient coating methods are continually being developed. Improved understanding of processes in the coating operation will lead to advances in the field of sugar panning in the next decades.

13.3.1.1 Revolving Pans

The standard revolving pan, either circular or tulip-shaped (Figure 13.4), is used quite extensively for all types of panning and polishing. These can be operated at speeds from about 15 to 35 RPM, with the choice of speed determined by the particular panning operation (size of pan, type of center, hard or soft panning, etc.). Some manufacturers control linear speed of the pan because it accounts for differences in pan size and thus, the forces on the tumbling pieces. The angle of the pan is typically between 18 and 30°, but this may vary slightly in some cases to promote ideal tumbling of the pieces. The shape and angle of tilt cause clumps of pieces that have stuck together to move forward in the pan where they are easily spotted and separated. Pan sizes vary from as small as 30 cm (12 in.) for lab-scale panners to as large as 1.5 m (5 ft) for the largest

Table 13.3 Parameters affecting sugar panning

Pan/center/dry charge	Syrup/air	Polish/glazing
Pan diameter	Application rate	Type of polish/glaze
Pan speed	Application method	Application method
Pan depth	Spray Pressure	Curing time
Pan load	Number of spray nozzles	
Pan size (tumbling height)	Spray nozzle size/orientation	
Center shape	Syrup temperature	
Center size/density	Syrup concentration	
Ribs (or not)	Syrup viscosity	
Center/pan temperature	Syrup composition	
Center precoating	Air flow rate	
Dry charge amount	Air temperature	
Dry charge size	Air humidity	
	Drying time	
	Air pattern (front or side-vent)	

Figure 13.4 Bank of traditional revolving pans for sugar panning(Courtesy of Georgia Nut Co.)

industrial sized units. Many commercial pans are 0.9–1.07 m (36–42 in.) in diameter.

The shape of the pans may also vary with the intended application. Circular pans cause more tumbling action and may be helpful to prevent doubles or clumping of centers with flat sides. Tulip-shaped pans, especially if elongated, hold more centers with increasing bed depth and thus, can handle larger batch sizes. Revolving pans, usually made from stainless steel or copper, can be used with a smooth interior or with ribs to promote tumbling of the centers as they are coated. Ribs are typically used during polishing to ensure proper tumbling of the centers, but may also be used to ensure adequate tumbling for certain types of centers. The drawback of using ribs for sugar panning is that crystallized buildup collects on the back side of the ribs. If this buildup breaks off it will stick to the centers and cause defects in the surface. When a ribbed pan is used for sugar shelling it will need to be cleaned more frequently to prevent this buildup from causing defects.

Panning in revolving pans is a batch operation with the entire process, from pre-coating to polishing, often taking place in the same pan, although some manufacturers use separate pans (and even separate rooms) for polishing. One pan operator is likely to be responsible for multiple pans making candies at the same time. The actions of the pan operator differ slightly for hard and soft panning.

13.3.1.1.1 Soft Panning

The operation for all soft-panned candies generally follows the same process (see Figure 13.5). After pre-coating the centers, a sugar shell is built up on the piece by sequential additions of engrossing syrup followed by dry powder charge. While there is a wide variation in formulations, typical composition of a soft panned candy can be 50–60% center, 30–35% dry charge sugar, 10–12% engrossing syrup and about 2% minor ingredients that include precoat, flavors, acid, colors, polish and seal coat.

The amount of centers loaded into the revolving pans depends on the size of the pan as well as the nature of the center. The correct fill of the pan is necessary to induce proper tumbling of the centers in the pan. If the pan is not adequately full, the centers do not tumble properly and will not be coated uniformly. If the pan is over-filled, there is the possibility that centers will fall out of the pan during the engrossing operation as they grow in size and weight. Furthermore, the added weight of the centers in a pan that is over-filled may cause deformation or even breakage of the centers. Panning speeds of 20–22 RPM are typically used in soft panning, although pan speed must be chosen to provide adequate tumbling forces, depending on pan size, to pack the dry charge into the engrossing syrup.

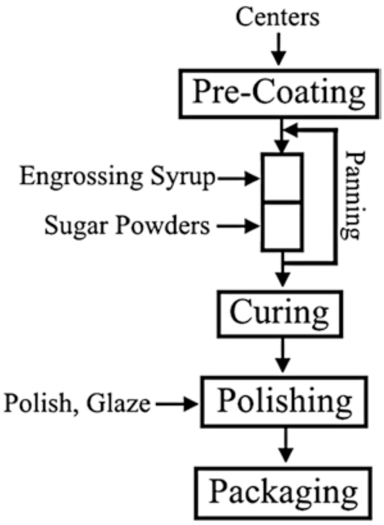


Figure 13.5 General flow process for soft sugarpanning

The soft panning process begins with pre-coating of the centers to ensure adequate adhesion of the sugar shell. For centers produced on a starch mogul, a sugar sanding step at the end of the mogul may serve as a sufficient pre-coat. For those centers that need further treatment, the pre-coat solution (usually gum arabic or dextrins) is applied to the centers, either by ladling or spray coating, as they tumble in the pan. This may be followed by addition of a small amount of dry charge, whether sugar crystals, starch granules or maltodextrin powder, to roughen up the surface to enhance adhesion of the sugar shell.

To build the sugar shell, the engrossing syrup (see Section 13.2.3.1) is applied either by hand ladling or by spray application. Engrossing syrup is added at a net total of about 10% of the weight of the centers in the pan, with individual wettings of 3–6%. If too much engrossing syrup is added at one time, the centers tend to stick together, forming doubles and larger aggregates. If the amount of syrup added is too low, the centers do not get uniformly coated and a rough surface is formed. The exact amount of engrossing syrup varies slightly from start to finish of soft panning since the center surface area increases as the shell is built up. Often, the amount of engrossing syrup to be added is left to operator judgment. Once ongoing production is commercialized, the amount is usually fixed to enhance efficiency and product uniformity.

Once a syrup layer has been applied and allowed to spread evenly on the surface of the centers, the dry powder charges are added. The amount of sugar powder added is crucial to building a satisfactory shell. Just enough powder must be added to dry out the newly applied layer of engrossing syrup. If too little powder is added, the layer is too wet and the centers stick together, whereas addition of too much powder results in excess powder in the pan. This can cause problems in later applications. The amount of powder to add is often left to the judgment of the pan operator, but again is usually fixed after production is commercialized. After addition of the first dry powder charge, the centers are tumbled until some of the moisture in the engrossing syrup is pressed to the surface by the force of contacts. This phenomenon is known as sweat-back, where the surface becomes moist again after sufficient tumbling. At this point, another dry powder charge, generally much less than the initial charge, is added. Again, the amount of powder to add is often left to operator judgment. The tumbling process continues and this dry charge addition becomes incorporated within the syrup of the sugar shell. Sweat-back may occur a second time and this must be followed with a third addition of dry charge. Eventually, no further moisture seepage to the surface occurs and the layer is considered complete. At this point, the next dose of engrossing syrup is added and the process of dry charge addition and sweat-back is repeated. In general, a ratio of three parts dry sugar charge to one part engrossing syrup is often used to build a soft sugar shell.

Over the course of the sequence of engrossing syrup applications, the nature of the dry powder charge added to the piece changes. In the early layers, coarser sugar powders may be used to quickly fill in and dry the layer. However, in the final layers, it is important to use the finest powdered sugar available to create the smoothest surface possible. Very fine particles can be packed much more tightly together than larger particles and leave a very smooth surface that, when polished, will give a very nice uniform smoothness to the piece. Regardless of the size of crystals in the dry charge powder, it is important that the particles be of uniform size with a minimum degree of dust. This allows proper packing of the crystals into the sugar shell and results in the best soft-panned texture.

Somewhere between three and ten layers (engrossing syrup charge plus dry powder charge) are applied on the centers with each layer taking roughly 20–40 min to complete. Thus, total panning time to apply the soft-panned sugar shell is from 2 to 4 h. Once the panning process is complete, the moisture remaining in the sugar shell is dependent on the moisture content of the engrossing syrup, how much engrossing syrup is applied in each layer, and the relative amount of powdered sugar charge to the amount of engrossing syrup. If the shell contains three parts dry sugar charge to one part of engrossing syrup with solids content of 76% (24% water), the sugar shell would have moisture content of about 6%. Typically, moisture content of the initial sugar shell is between 4% and 8%.

Proper panning room conditions are needed to ensure a high-quality panned product. Room temperature should be around 21 °C (70 °F) with relative humidity less than about 55–60%. Warmer temperatures and high relative humidity make it difficult to adequately build up a sugar shell with the correct moisture content. Cooler temperatures cause the viscosity of the engrossing syrup to increase, potentially causing uneven coatings.

The end point of panning is often determined by weight. If a pan is on load cells, the engrossed weight is easily calculated as a multiple of the starting weight of centers. When load cells are not available, a count of 10–50 centers is weighed at the beginning of the process and the weights are repeated near the end of the process to identify the finished target piece weight. Once the desired shell thickness is attained by sequential addition of engrossing syrup and dry powder charge, the pieces are removed from the pan, filled into a tray and allowed to sit overnight. The resting time allows moisture to equilibrate between shell and center. The next day, the centers are placed back in a pan and several applications of a finishing syrup are applied to smooth the surface and dissolve any dust. Once the surface is dry after smoothing, layers of wax and/or polish and seal coat are applied. Once polishing and sealing is complete, the pieces are sent to packaging.

Soft-panned candies can also be made with dextrose and polyol (sorbitol, maltitol, xylitol, isomalt, etc.) shells in essentially the same manner as for sucrose. The engrossing syrup must be essentially noncrystallizing and fine powdered sugars added in the dry charge steps. For glucose, the engrossing syrup typically contains soluble dextrose and dextrose syrup and the process is exactly the same as for sucrose panning. For polyols, typically HSH or maltitol syrups are used in the engrossing syrup along with the dissolved form of whatever polyol powder is used in the dry charge.

13.3.1.1.2 Hard Panning

The application of a hard sugar (or sugar alcohol) shell in hard panning requires determined practice and patience. Many candy makers still consider the hard panning process to be somewhat of an art, yet our understanding of the processes occurring during hard panning continues to expand as more and more of the science behind panning is applied. In general, experience and practice is still the best approach to becoming an accomplished panner.

The general steps in hard panning are pre-coating of the centers and application of sequential doses of the coating syrup each followed by a period of drying to ensure crystallization of the shell (see Figure 13.6). Once the shell is built up to the desired thickness, the pieces are allowed to rest overnight before polishing and glazing the next day. The sequence of syrup addition and drying is critical to making the highest quality hard panned candies.

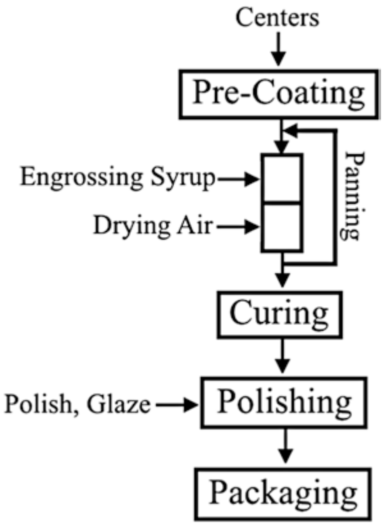


Figure 13.6 General flow process for hard sugar panning

In hard panning, the centers generally must be pre-coated to ensure a high quality sugar shell. If centers like chocolate and nuts are not pre-coated, the oil phase at the surface of the piece prevents adhesion and the shell is easily broken away. Pre-coating typically involves application of a gum (e.g., gum arabic) or maltodextrin layer, often followed by addition of a powder (i.e., sugar, starch or flour) to provide a layer suitable for adhesion of sugar syrup.

Once pre-coated, the centers tumbling in the pan are coated with a sugar solution of proper viscosity, temperature and concentration. Enough syrup is applied to give a layer of syrup to provide a uniform coating on all pieces, which depends on the surface are of pieces in the pan. If too much syrup is applied, the syrup is transferred to the back of the pan and sticking occurs. It has been estimated that a layer with thickness between 10 and 15 μm is created with each wetting. The engrossing syrup must have the appropriate viscosity to adequately cover the surface of the piece. If viscosity is too high, the pieces do not get completely covered and bare spots will be present. Too low a viscosity generally means that there is excess water in the syrup and this water must be evaporated during drying to promote proper crystallization. Cycle times between syrup applications may be longer when concentration is too low. Typically, the time for each application of syrup and drying cycle is between 5 and 10 min, but this time depends to some extent on environmental conditions, with longer drying times needed for more humid environments.

Sugar syrup viscosity is primarily a function of the temperature and concentration, so controlling these two parameters is generally sufficient to controlling viscosity of the engrossing syrup. The concentration of the syrup should be sufficiently high to minimize the amount of water that must be removed during drying and to promote rapid crystallization, but not too high that excessive viscosity limits the ability to form a uniform coating. Often, a value of about 200 cP is cited as the maximum viscosity for the engrossing syrup in hard panning (Boutin 1992). The temperature of hard panning is governed by the thermal sensitivity of the center. If a temperature-sensitive center, like chocolate or gum, is used, panning temperatures must remain below the softening point. For chocolates, syrup temperatures must be below about 30 °C (86 °F), which is about the same temperature for gum centers. Centers that are not sensitive to temperature can be hard panned at temperatures of 70–80 °C (158–176 °F). In fact, hard sugar panning of certain heat-resistant centers can be done with heat applied directly to the pan to speed drying and crystallization. For example, Jordan almonds are traditionally made in the hot pan process with heat applied to the pan.

After the engrossing syrup is applied, the centers are allowed to tumble for a short while to completely distribute the syrup and coat the centers. At this point, drying air is applied to the centers to promote drying and crystallization. To control drying and crystallization, air parameters must be carefully controlled. Sufficient air velocity across (and/or through) the entire bed of candy 0.00042–0.00057 m^3/s (0.9–1.2 ft^3 per min) per pound of finished product is required to remove the moisture in the engrossing syrup as crystallization occurs. Drying air generally should be as warm as possible, within the limitations of heat-sensitive centers, with low relative humidity (25–45%). Once a layer has completely dried and crystallized, another dose of engrossing syrup is added and the cycle repeated.

The decision point for adding the next dose of sugar syrup is one that is often operator dependent. The usual cues are when the previous layer dries sufficiently to cause a change in sound as the pieces tumble across each other (dry pieces give a different sound than wet pieces), and when a slight dust begins to arise from the pan. When the shell dries sufficiently, small pieces of the shell, which appear as dust, are broken off by the tumbling action in the pan. At the first signs of dust and sound change (from quiet while wet to a tinny, pinging sound of dry pieces tumbling), the experienced operator will apply the next layer of sugar syrup.

To build up a suitable thickness of shell with hard panning requires care and patience. In many hard-panned candies, 40–60 syrup applications (and drying cycles) may be needed to build a shell thick enough, so that it takes over 6 h to build the shell. Some hard panned products, like jawbreakers, require over 300 layers so that it may take a week or two of careful syrup application to build the product to the desired size. Patience is certainly an important attribute for a pan operator making these products.

For centers that are not heat sensitive, a hot panning technique may be applied. Here, the syrups are warmed to temperatures well over 39 °C (102 °F) and additional heat is applied to the pan to warm the centers. Although a gas flame aimed at the bottom of the pan is the traditional method, heating is generally from hot air directed into the pan or steam coils wrapped around the pan. Advantages of hot panning include use of a higher concentration engrossing syrup (higher temperatures allow higher concentration with reduced viscosity) so less water needs to be dried off, more rapid crystallization at the elevated temperature and more rapid drying. Jawbreakers and Jordan almonds, as well as sugar-coated tablet candies can benefit greatly from the more rapid cycles in hot panning.

Because of the long times needed to build up a hard-panned sugar shell, sometimes short cuts are taken to reduce batch times. In particular, a modified soft-panning process may be used in the early stages of hard panning to rapidly build a shell. Here, a dried powdered sugar charge, generally mixed with starch, is applied immediately following application of the engrossing syrup, which may contain cellulose gum, in a similar process to soft panning. This technique is frequently called dry charging. The addition of sugar powder to the engrossing syrup speeds the build up of the shell and the presence of gum and starch helps harden these layers. Although the texture of the hard-panned shell is not as brittle, if done properly, batch time can be reduced significantly (up to 60%) with minimal loss of quality.

Towards the end of the hard-panning process, as the shell nears its final thickness, the engrossing syrup is changed slightly to ensure a smooth surface. Lower dissolved solids (less than 65%) in the engrossing syrup help to create a smooth surface. The higher water content ensures uniform coverage (due to the reduced viscosity) and dissolves some of the crystals in the previous layer, allowing "low points" in the coating to get filled in. Upon drying, an exceedingly smooth surface with minimal perturbations is formed. This results in uniform color intensity and a shiny appearance.

Not all hard panning syrup applications contain colors. In some cases, manufacturers do not add color except to the final coating layers. Color coats are applied in the same way as previous applications, but with color added to the engrossing syrup as either lakes or dyes. To enhance visual color appearance, many manufacturers add titanium dioxide to all or some of the underlying sugar shells. The titanium dioxide particles reflect the light that passes through the color layers, giving a fuller and deeper color than would otherwise be observed.

Once the desired sugar shell has been built up, the candies are stored in cool dry conditions to allow the shell to solidify completely (residual sugar crystallization occurs) and the moisture within the shell to equilibrate. The candies are often stored overnight in shallow trays under cool and dry conditions before being returned to the pans for polishing and glazing.

Although sucrose remains the most important sugar used for hard panning many other sugars can be used. These include dextrose, sorbitol, xylitol, maltitol and isomalt. In general, the processes for hard panning with materials other than sucrose follow an identical process of application of engrossing syrup followed by a period of drying. The main differences in hard panning among the different sweeteners relate to differences in viscosity and the nature of crystallization (rate and type of crystal formed). For example, a concentrated solution of dissolved dextrose is less viscous than an equivalent concentration of sucrose (monsaccharides are less viscous than disaccharides) so higher concentrations can be used for dextrose panning. Dextrose also crystallizes very rapidly into numerous tiny crystals that result in a strong hard shell. Further, dextrose crystallizes as a monohydrate during panning, meaning one mole of water enters the crystal lattice with each mole of glucose, so that correspondingly less water needs to be evaporated from the shell during drying. These effects are also greatly enhanced in hot panning. Dextrose also has a larger positive heat of crystallization than sucrose (see Section 2.3), which provides additional driving force for drying although the released heat must be removed by the drying air (greater cooling effect needed). Additional details on dextrose panning can be found in Horn (1977), Boutin (1988), and Nonaka (1991), while sugar-free panning is explained in further detail by Boutin (1992) and Huzinec (2010).

13.3.1.2 Other Coating Technologies

Over the years, new developments have improved the panning process, making them more automatic and less subject to human variability (Boutin, 2012). One type of coating device often used for panned candies is the belt coater, where the centers are tumbled on a continuous belt while being coated with engrossing syrup from spray nozzles above the bed of candy. High production, fully automated panning systems are also available. Film coating technologies, borrowed from the pharmaceutical industry, may also be used to apply candy shells.

13.3.1.2.1 Belt Coater

Belt-type pan coating systems are most often used for chocolate panning (see Chapter 16), but see some application in soft panned (jelly bean) applications. They operate in a slightly different fashion from the traditional revolving pans. In the belt coater, the pieces to be coated are tumbled by movement of a continuous belt, as seen in Figure 13.7. In this case, the candy pieces are contained within a depression in the continuous belt and the movement of the belt results in uniform tumbling. In this geometry, the entire front of the candy bed is open and available for engrossing syrup application. Sugar syrup is applied across the top of the pieces in the tumbling section. Belt coaters can be 1.5–4 m wide and hold upwards of 300 kg (650 lb) of centers.

One of the main advantages of the belt coater is the level of automation that can be applied. Computer controllers can automate the process and reduce the need for manual labor. Furthermore, unloading of the belt coater is easily accomplished by reversing the direction of belt rotation, with pieces collected in trays or bins at the front of the unit. Facilitated removal of drying air and/or volatiles during polishing through the exhaust system allows more efficient operation than a traditional pan. In general, more efficient operations are found with the belt coater and productivity thereby increased.

Figure 13.7 Belt coater (Courtesy of Driam)

13.3.1.2.2 Cylindrical Drum Panning Systems

In large-scale hard panning operations, it is often most efficient to use fully automated panning units (Figure 13.8). These are typically enclosed cylinders or drums inside which the tumbling candy pieces are coated. The candy pieces tumble inside the drum and are coated with sugar syrup from spray nozzles positioned within the rotating drum (Figure 13.9). Drying air is usually vented through one end of the pan, with air flow either across the pieces and out the other end of the drum or directly through a perforated drum in automated closed-system designs. The improved air handling systems give excellent heat and mass transfer, resulting in very rapid and efficient panning. Cylindrical drum panning systems can handle from 225 kg (500 lb) to 2,700 kg (6,000 lb) of product.

Computer automation of the sequenced steps in panning means high efficiency and increased

Figure 13.8 Drum coater for hard panning (Courtesy of Dumoulin)

Figure 13.9 Sugar spray system inside drum coater (Courtesy of Dumoulin)

productivity. In some cases, detection methods (e.g., moisture content) may be used to determine onset of specific operations.

13.3.1.2.3 Continuous Panning

As a batch operation with intensive labor requirements, panning is an inherently inefficient operation. For many years, people have attempted to develop continuous panning operations to enhance process efficiency. In continuous panning, uncoated centers entering one end of the process and finished panned goods exiting the other end. The sequence of events in the continuous panner simulates the sequence of events found in the batch process. For soft shell panning, continuous panners have been designed to continuously move the centers from section to section, with sequenced dosing of engrossing syrup and powdered sugars as the pieces move from the inlet of the drum to the outlet. Their application has thus far been limited to relatively hard centers with thin coatings (15–25%). As the application of sensor automation improves, the applications for automated soft panning will increase.

Although in principle, continuous coaters can potentially provide efficiency in operation by controlling all panning conditions, cost is often prohibitive, particularly in a manufacturing plant that changes product regularly. These would be most advantageous for large production runs of the same product.

13.3.1.3 Candy Center Motion and Scale-Up

Candy centers tumbling in a pan are subject to various forces depending on the type of product, type of pan, and the operating conditions. As noted in Table 13.2, parameters such as pan or drum diameter, rotational speed, bed depth and weight, center size and density, and center surface roughness can all impact how the centers move during pan rotation. These parameters define the movement of each individual candy piece within the bed. Of primary importance to getting good uniform surface coverage is that each piece be exposed at the surface of the tumbling bed for about the same amount of time during application of the engrossing syrup. Whether ladling or spraying the engrossing syrup onto the bed of candy centers, each piece must receive the same amount of syrup coverage or there is a risk of uneven, bumpy and inconsistent product.

Another concern related to pieces tumbling in the pan is segregation of centers of different size, shape and weight. In tulip-shaped pans in particular, the angle of the pan imparts a downward force on the piece so pieces of different size and weight fall at a different speed, leading to segregation. In general, centers of approximately the same size and weight must be used in pans to ensure uniform mixing of centers. Where segregation is most likely to occur is when doubles or multiples are formed. If, for example, too much engrossing syrup is added at one time, centers are likely to stick together to form multiples. These have larger mass than the single pieces and thus are driven to the front of the pan by the tumbling forces. Even pieces of different shape can experience sufficiently different forces that these are segregated from the main bed in the same way.

Primarily because of these variations in tumbling forces, panned candy developers are continually looking to better understand how to design a product in lab bench panners and scale the process up to commercial-sized pans. The variety of forces important during panning, particularly when increasing the size of the pan and the mass of the candy in the pan, means that scale-up is no simple task. In concept, successful scale-up generally requires geometric, dynamic and kinematic similarity between the smaller and larger size equipment (Pandey et al. 2006). In panning, geometric similarity means panners with similar aspect ratios (pan length to diameter) and also maintaining a constant pan load to pan volume. Without geometric similarity, scale up will be difficult, if not impossible. Dynamic similarity is attained with a constant ratio of inertial forces (due to the rotational speed of the pan) to gravitational forces. Inertial forces are related to the pan's rotational speed and diameter since the pieces move at the same speed as the inside wall of the pan. To maintain dynamic similarity in panning means that pan rotational speed must be decreased as pan diameter increases; this best related to the linear speed at the pan surface (which is what moves the pieces). Kinematic similarity, where the ratios of the velocities of the important factors at different points in the pan is maintained constant between the different scales of operation, is probably the most difficult aspect of scale up for panning operations. Pandey et al. (2006) suggested that, for hard panning operations, the velocity of the tablets (pharmaceuticals) relative to the engrossing syrup spray kinetics should be kept the same, but this concept will not always apply in confectionery panning (especially with hand application of engrossing syrup). They also recommended maintaining constant drying capacity (ratio of airflow to spray rate). For example, in a larger pan, typically the time a piece is in contact with the spray zone is reduced, which means that the effective drying time in larger scale operation is longer. To offset this, the spray zone should be expanded by a combination of changing air velocity in the spray mechanism, increasing the number of spray guns, and adjusting the distance from the spray gun to the tumbling bed. Based on this discussion, it is not surprising that scale up of confectionery panning operations is quite a complex challenge.

13.3.2 Polishing and Glazing

Most panned candies, whether hard or soft sugar coated, are polished and glazed to protect the candy and to give it an attractive, shiny appearance. Polishing is the process of applying a shine to the candy and is followed by glazing with a protective barrier to maintain product quality.

The main purpose of a polishing agent applied to a panned candy is to create a smooth, glossy surface. In doing so, often the color of the piece is also enhanced. The polished candy is significantly more attractive to the consumer than an unpolished piece. Application levels of polish to panned candies are from 0.05% to 0.3% for sugar-panned candies and from 0.4% to 0.8% for chocolate panned products. The main purpose of a glazing agent applied to a panned candy is to protect and seal the surface from the environment, primarily against high temperatures (at least to some extent) and moisture sorption. The sealed surface also prevents pieces from sticking together in the package during shipping. Application levels of glaze are from 0.1% to 0.3%.

Polishes for sugar-panned candies are primarily waxes, including carnauba and beeswax. Waxes are applied either in solid form, with the heat of friction during tumbling allowing the wax to spread and coat, or as a solution in an organic solvent (e.g., alcohol). Glazes are generally shellac in a solvent carrier. Alcohol is the main solvent for glazes, but other solvents are sometimes used because of environmental (volatile organic compounds, VOC) concerns (consult with the pertinent emission guidelines to ensure the process is within code). Single-step coatings that combine wax and shellac in a solvent are also available for use.

Prior to polishing, sugar-panned goods should be fully dried, free from dust and perfectly smooth. In soft panning, the final layers should be packed with the smallest possible grade of crystals to ensure the smoothest finish. It is important to apply a finishing syrup to soft panned goods to smooth out the surface and remove any dust prior to application of the polish. In hard panning, reduced concentration engrossing syrups ensure that the final smoothing layers are as even as possible. It is critical that the panned candies have been allowed to fully dry and crystallize. Often, this means the candies have been stored overnight under controlled conditions (RH and temperature) to ensure complete solidification and moisture equilibration.

The candies to be polished are tumbled in a revolving pan, most often fitted with ribs to enhance the tumbling motion. First the polishing agent is applied to the pieces tumbling in the pan to just wet the surface and this is allowed to dry, usually without the use of drying air unless relative humidity is high (above 60%). A second coat may be added in the same way and allowed to dry. After the final coat has dried, cooling air may be used on the tumbling pieces to develop a deep shine.

Polishing gives an attractive appearance to the panned candy, but does not sufficiently protect the candy from extreme heat and humidity during storage. Thus, many companies choose to apply a glazing agent to the candy for enhanced protection. Prior to application of the glaze, the polished candy should be thoroughly dried, sometimes by storing overnight in cool, dry conditions. It is important to ensure that the pieces are free of dust prior to glazing. The pieces are once again placed in a revolving pan fitted with ribs to enhance tumbling. A glazing solution containing edible shellac dissolved in alcohol is applied to the candy pieces. In some cases, drying of the glaze is done with the pan rotating, but in other cases, static drying is preferred. With static drying, after the pieces have been coated with the solution, the pan rotation is stopped and the glaze allowed to dry under static conditions. The pan is turned about one-half revolution, or jogged, two or three times during the 20–30 min it takes to dry to prevent tack spots from forming. After complete drying, the pieces are tumbled briefly to smooth out the surface.

13.3.3 Special Decorations

Special and unique characteristics can be imparted to panned candies (Gesford 2001). These include pearling, striping, decorating, and silvering. In soft-panning, it is even possible to include particulate inclusions in the sugar shell. It is quite possible that several of these special techniques were discovered by accident, where a "mistake" turned out to have unique and interesting qualities. Many panned candies also have words or logos printed on them to help distinguish them from competitors.

Pearling is the process of intentionally building an uneven surface to a hard-panned candy. Japanese confectioners have become particularly adept at this process, with a unique sugar candy available based on this process. Use of elevated panning temperatures, typically controlled by adding heat to the bottom of a rotating pan, and high concentration engrossing syrups lead to rapid drying and crystallization, even before the syrup can be spread uniformly on the center surfaces. This high concentration and temperature cause nodules or protuberances of thickened, partially-crystalline and sticky syrup to form on the candy surface, particularly as the pieces come apart during tumbling. With careful control of operating conditions, these protuberances are allowed to grow as further additions of engrossing syrup are applied. The result is an irregular surface that can vary from slight dimpling (like the surface of an orange) to the appearance of nodules or spikes several millimeters in length, in the extreme case.

Stripes, or narrow light and dark lines, similar to longitude lines on a globe, provide a unique appearance to sugar-panned goods. Striping is more about the nature of the center than it is about panning techniques. A center with a grooved surface, such as gum or a tablet, holds the engrossing syrups at different thicknesses in the grooves than on the flat surfaces. Thus, the grooves appear to be a darker color than the flat surface and the candy appears striped.

To create a spotted or speckled appearance to the surface of a sugar-panned candy, whether hard or soft panned, a colored solution is either spattered or sprayed onto the finished surface prior to polishing. In one version, an organic solvent like alcohol is used to disperse the color to ensure rapid drying as the solvent evaporates off. Water soluble colors are unsuitable since the water in the solvent would dissolve some of the sugar shell and could potentially remove the base color. Another method of spotting/speckling involves application of a colored, aqueous-based film-forming material (gums, maltodextrin, dextrins, etc.), which quickly dries and sets upon application of heat. Speckling can also be accomplished during polishing, with color pigments incorporated into a confectioner's glaze.

Certain types of decorative hard-panned candies are given a silver metallic finish through a process called silvering. To make silver balls, a gum arabic solution containing silver leaf or powder is applied to the candy while tumbling in a pan (often glass or plastic pans are used to prevent tarnishing of the silver surface). As the moisture in the syrup evaporates, a layer of silver forms on the surface of the candy. Extensive tumbling is needed to prepare a highly polished surface. Silvering is legal only for decorative purposes in the United States.

Certain sugar-panned candies have logos imprinted on the surface of the sugar shell. Typically imprinting is done to establish brand identity, although, recently sugar panned candies are now available with custom-printed slogans, often designed for special occasions (weddings, holidays, etc.). Printing on a sugar shell involves application of edible ink to the surface of the candy. Edible inks typically contain pigments in an alcohol and shellac base, with other additives to moderate the properties of the ink. The rotogravure process, which uses an offset roller to apply the ink, is the most common method of printing on sugar shells. Here, the ink is applied to the lettering on the offset roller, which then contacts the candy with the application surface presented to the roller. The ink is allowed to dry before the candy piece is removed from the conveyor. Recent developments with ink-jet printing technology using edible inks are allowing more sophisticated designs.

13.3.4 Multicomponent Layering

By its nature, soft panning is essentially creating a solid dispersion on the surface of a center. In the classic sense, this is thought of as a syrup phase holding together sugar crystals. For someone experienced in the art of panning, it is clear that the same principles can also be used to create other types of coatings. The addition of calcium carbonate can be used to create a coating that resembles an egg shell. Fruit powders or seeds can be added to make products that more closely resemble fruit. Fibers, vitamins, or other nutraceuticals can be added to create nutritional supplements. Milk or yogurt could be added for their flavor and mouth feel. It is also possible to create distinct layers with a product. For example, a center could first be coated with chocolate and then a sugar layer. A combination of fat, cocoa, and sugar could be added to make a chocolate-like layer in place. Similarly combinations of dairy and carbohydrate ingredients can build a caramel layer into a product. Colloid ingredients can build a jelly layer into a product. A cherry can be coated with sugar, some invertase enzyme, and then chocolate. Once the invertase converts the sucrose to invert syrup, a perfectly round, liquid filled chocolate covered cherry will impress confectionery connoisseurs. Any dispersion of ingredients can be combined in place to produce a layer on or within a product.

13.4 Product Characteristics

As with most confections, sugar panned goods require careful control of water and the state of the sweeteners to ensure optimal quality. The nature of the microstructure, or sugar crystal dispersion (size, number, interconnectedness, etc.), is what determines the texture of the shell and distinguishes between hard and soft panning. In turn, the nature of the sugar crystals is controlled by the formulation of the engrossing syrup, including water content, as well as panning conditions such as. Equilibration of water within the sugar shell and between the various components of panned candies also affects product texture and quality. Changes in water content during storage are often what limit the shelf life of panned confections.

13.4.1 Microstructure of Panned Sugar Shells

The characteristics of hard panned sugar shells are quite different from soft panned shells, particularly related to the number, size and shape of the crystals. Differences in microstructure lead to the different textures of hard and soft-panned candies. Both formulation of the engrossing syrup and panning conditions influence the nature of crystalline microstructure and thereby influence shell texture.

13.4.1.1 Soft Panned Candies

The sugar shell on soft-panned candies is made up of numerous, relatively large crystals, typically from 25 to perhaps 100 μm in size depending on the dry charge added during panning. These crystals are packed into a fluid binder, the engrossing syrup, which holds them together (as shown schematically in Figure 13.1). The tumbling forces in the pan pack the crystals tightly into the syrup layer. Figure 13.10 shows stereomicroscopic cross sections of a soft-panned candy at different magnifications. Individual crystals can be distinguished in this shell, with these crystals held in place by the sugar syrup matrix. This relatively loose structure of large crystals breaks readily under applied force, giving the soft, easily broken texture of a soft-panned sugar shell. Characteristics of the soft-panned sugar shell depend on the nature of the engrossing syrup, the types of sugar powders added during panning, and changes that occur as the shell cools and equilibrates after panning is completed.

The nature of the sugar powders used to build the soft-panned sugar shell significantly effects shell characteristics. Typically, larger crystals give a softer, easier to bite texture, but one that feels coarser in the mouth. When external force is applied to bite through a soft-panned candy, the shell breaks at the weakest points. Larger crystals give fewer junction points between particles (compared to numerous small crystals), making it

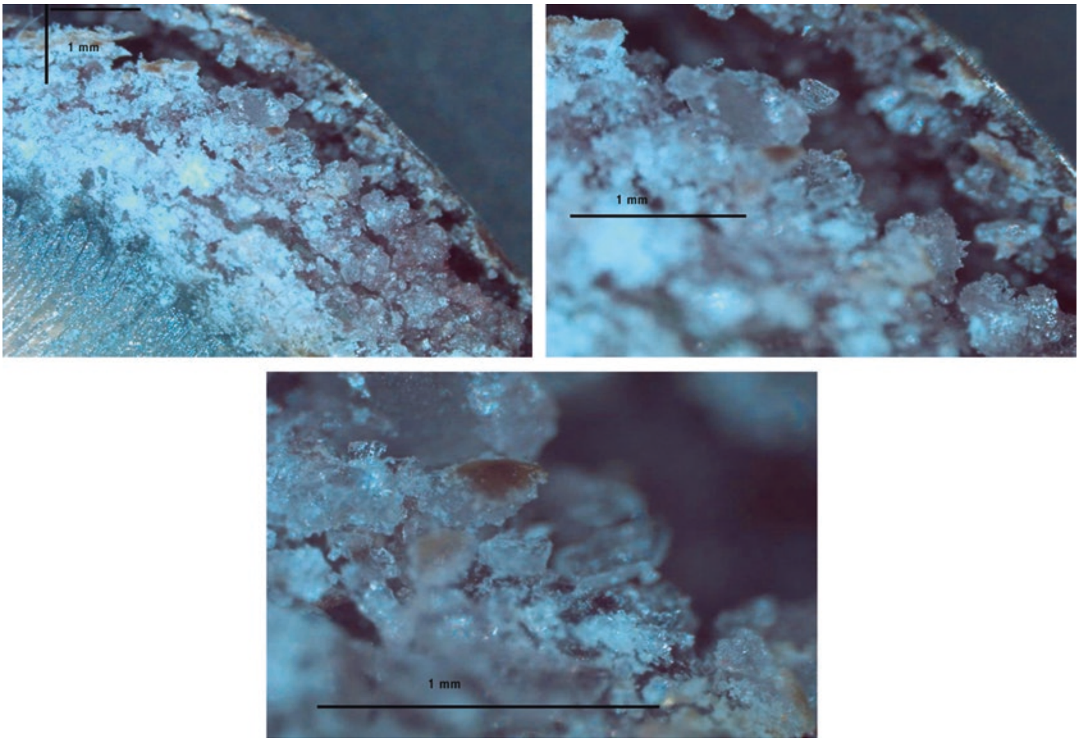


Figure 13.10 Stereomicroscope image of cross-section of soft-panned candies (Pictures courtesy of P. Gesford)

relatively easy to break through the layer. Thus, finer powders give both smoother finish and firmer texture to a soft-panned confection.

However, when bridges form between adjacent crystals, the force required to break through the sugar shell increases substantially. Thus, anything that causes bridging between crystals results in a harder shell. For example, the changing water content of the sugar shell, either during curing (stoving) or storage, results in sugar crystallizing out of the engrossing syrup solution. Since sugar crystallizes under these conditions directly onto existing crystals (rather than forming new nuclei), the crystallization that occurs when the sugar shell dries out leads to crystal bridge formation between adjacent particles. Not only does the lower moisture content mean there is more crystalline mass, any bridged crystals that have grown together also resist breakage. The result is a harder shell.

Temperature changes during processing can also lead to crystal bridging. Although the engrossing syrup is generally considered to be noncrystallizing in soft panning, this is not always entirely true and any crystallization from the engrossing syrup during cooling can induce bridging between crystals. In general, a small amount of crystallization does indeed occur from the engrossing syrup, with the extent dependent on composition and panning temperature. This can be seen from the effect of temperature on the solubility curve of sucrose in the presence of glucose syrup. As shown in Figure 13.11, the solubility of sucrose in a solution with glucose syrup decreases with temperature. The extent of crystallization as a 50:50 solution of sucrose and glucose syrup (saturated at 50 °C with 195 g of each per 100 g of water) cools to 25 °C can be seen as the amount of sucrose that must crystallize out of solution during cooling. At 25 °C, the concentration of sucrose in a saturated solution containing 195 g glucose syrup/100 g water is only about 145 g sucrose/100 g water. Thus, about 50 g sucrose/100 g water must crystallize from the engrossing syrup to maintain phase equilibrium. This crystalline sucrose forms on existing crystals (from the dry powder charge) causing all crystals to get slightly larger, but also causing bridging between adjacent crystals in the shell. Thus, panning under conditions where the engrossing syrup is applied warm results in significant sucrose crystallization and bridging, the result of which is a slightly harder shell (although still nowhere near as hard as a hard panned shell). Further, the engrossing syrup will often dissolve some of the dry charge, resulting in a changing saturation level of the engrossing syrup during panning.

13.4.1.2 Hard Panned Candies

In contrast to soft-panned sugar candies, the shell of a hard-panned candy is made up of numerous very small sugar crystals that are bonded together in some fashion, as shown schematically in Figure 13.2. Figure 13.12 shows the cross-section of a hard-panned sugar shell at different stages

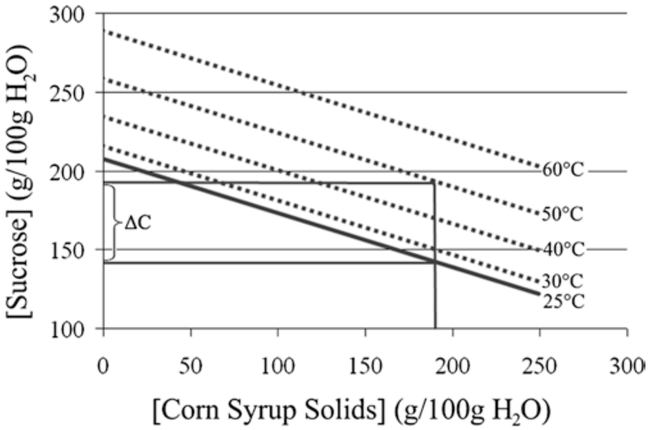


Figure 13.11 Effect of temperature and glucose syrup content on solubility concentration of sucrose

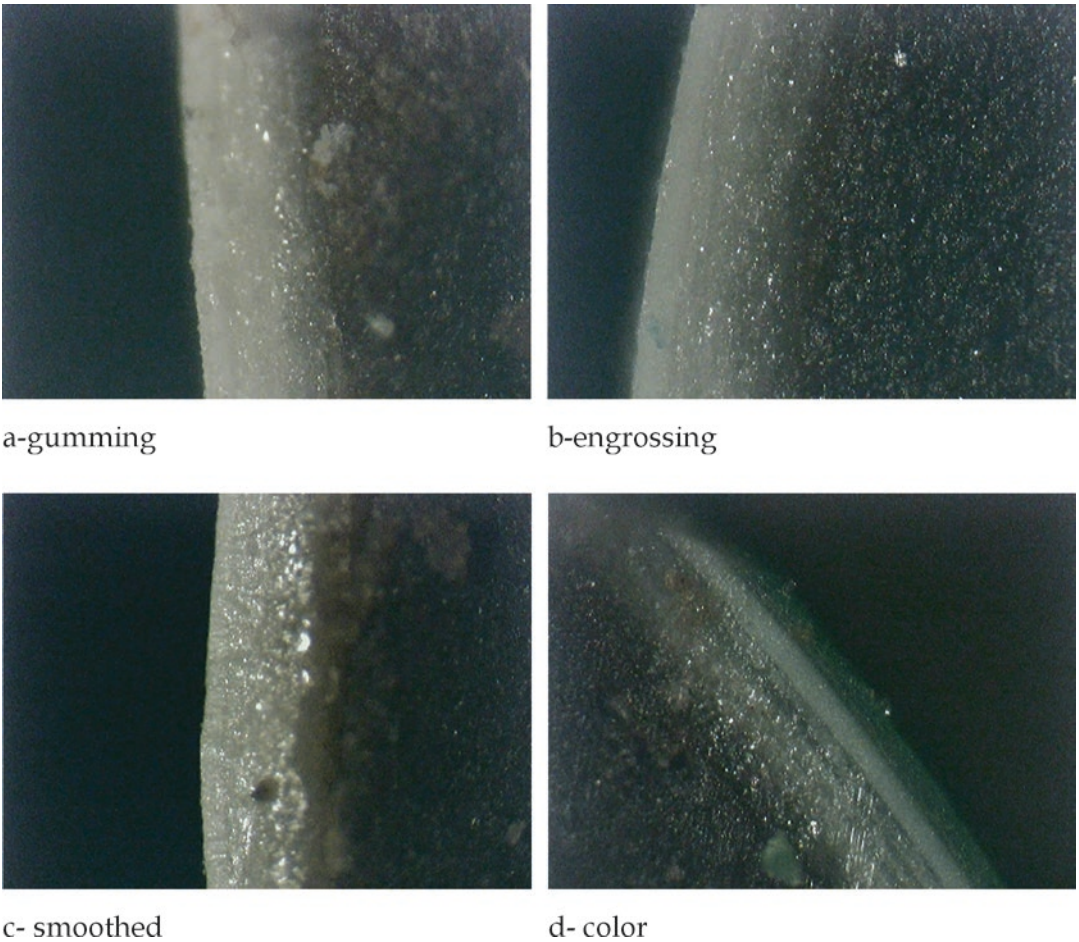

a-gumming b-engrossing c- smoothed d- color

Figure 13.12 Cross-section of a hard-panned sugar shell at different points in the panning process (Courtesy J. Bogusz)

during production. Careful inspection of these cross-sections shows the different layers (gumming, engrossing, smoothing layer, color layer). Although not distinguishable at these magnifications, the hard-panned sugar shell contains numerous small (probably less than 1 μm) crystals, likely bridged together, held in place by a small amount of saturated (sucrose concentration of ≈67% at room temperature) solution with very low water content (<3–4%).

The microstructure of the hard-panned sugar shell depends on multiple processes that occur during panning. After application of the engrossing syrup, the fluid must be uniformly spread across the surface of the centers, after which both crystallization and drying occur as the layer solidifies. It is the relative rates of crystallization and drying that determine the microstructure and texture of the hard-panned sugar shell.

13.4.1.2.1 Crystallization Versus Drying

Arguably the most critical aspect of hard panning is controlling sugar crystallization in each cycle. Once the engrossing syrup is applied, both crystallization and drying start immediately, with each process affecting the other. Controlling these processes is critical to creating a good sugar shell with desirable properties.

In a sense, drying and crystallization are competitive processes since one (drying) leads to an increase in dissolved solids and the other (crystallization) leads to a decrease in dissolved solids in

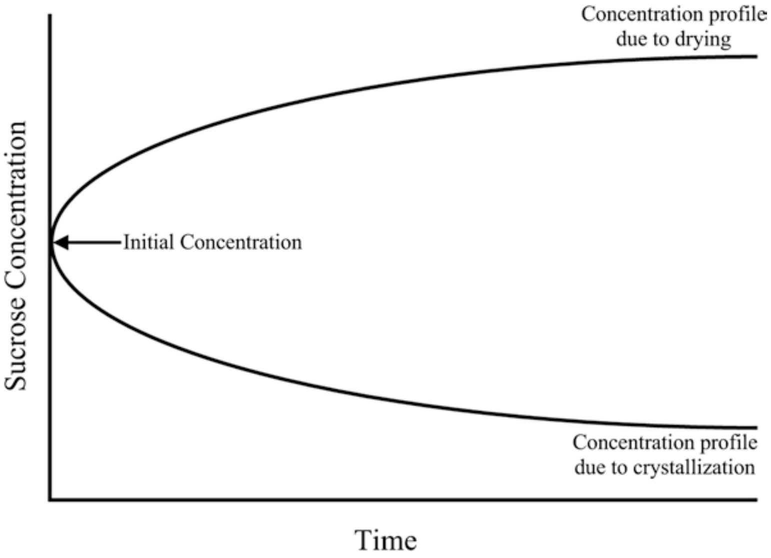


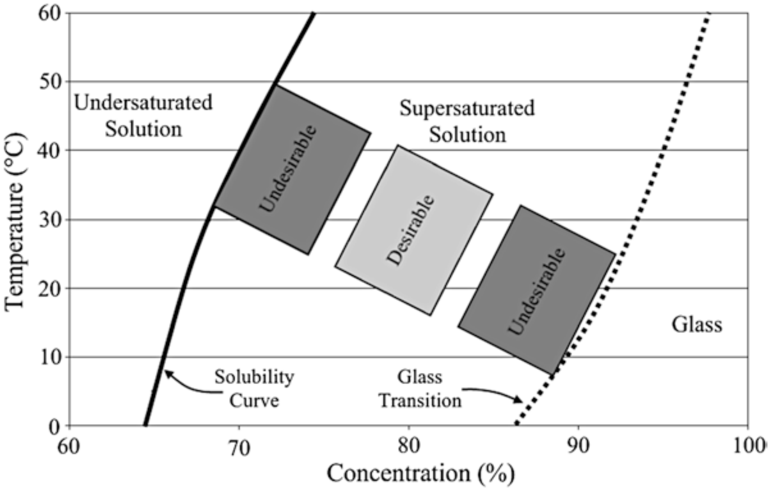
Figure 13.13 Schematic diagram of effects of drying and crystallization on liquid phase concentration

the syrup as molecules are removed from the liquid phase into the crystalline solid. As seen in Figure 13.13, drying causes an increase in solution concentration as water is removed from the film, whereas crystallization causes a decrease in liquid phase concentration as sugar molecules leave the liquid phase to become crystals. In crystallization terms, this decrease in the solution phase concentration is called desupersaturation, which continues until the supersaturation reaches zero at the point when solution concentration reaches the solubility concentration for that system and temperature. Thus, drying and crystallization "compete" in terms of the trend in the solution concentration. Drying leads to increased concentration while crystallization leads to lower concentration.

Yet, each process affects the other since the rates of drying and crystallization depend on the solution concentration and its water activity. For drying, the driving force is the difference in moisture between the air (relative humidity) and the water activity of the wet engrossing syrup layer, which is related to moisture content of that layer. For crystallization, the driving force for crystals to form and grow is proportional to the difference between the actual solution concentration and the solubility concentration at that temperature. Thus, the concentration of the engrossing syrup layer at any point in the process determines the rates of drying and crystallization. In one extreme case, for example, if drying were sufficiently rapid, the sugar solids would increase rapidly to the point where it became glassy and no crystallization would occur (see Section 2.11). Thus, the rate of drying can significantly impact the rate of crystallization (and vice versa).

To promote rapid crystallization of the sugar shell requires that the applied syrup rapidly reach the optimal point of nucleation/growth on the state diagram (see Section 2.2 for more details). The syrup layer should not be too concentrated, where mass transfer is limited by the glassy state, or too dilute, where the supersaturation is too low to promote rapid crystallization. Figure 13.14 suggests a region on the state diagram, somewhere midway between the solubility line and the glass transition curve, which promotes maximal crystallization during hard panning. Thus, both the concentration of sugar in engrossing syrup layer and the temperature during panning are critical to rapid crystallization. Directly after application of the sugar syrup, it would be desirable for the sugar solution to reach a point on the state diagram that resulted in a high rate of nucleation, leading to the numerous small crystals desired for the hard, brittle shell. Once nucleation has been initiated, drying can begin in earnest (some drying is inevitable as soon as the syrup is applied to the center) to remove the water in solution. Drying should not occur so rapidly,

Figure 13.14 Range of desired conditions for satisfactory hard panning



especially early in the cycle, that crystallization is impeded. If done correctly, drying and crystallization occur in concert so that crystallization is nearly complete when the layer has been dried sufficiently for the next syrup application.

The final remaining crystallization, to attain equilibrium between crystal and liquid phase, may take days to complete. Thus, the sugar shell on a hard panned candy after it has just been removed from the pan is slightly softer and less brittle (almost wet) than the end product after several days of equilibration. During this equilibration process is most likely when fusion of crystals occurs to give a hard, brittle texture at the same time the shell equilibrates with the center and with the surrounding ambient air. This can be detected physically as a distinct hardening of the shell over time.

Factors that affect drying include air circulation velocity, air temperature and relative humidity. In general the rate of drying is promoted by an increase in velocity and temperature and a decrease in air humidity. High air circulation rates mean that the air passing across the wet engrossing syrup layer can more efficiently remove moisture through the higher convective mass transfer coefficient. Higher air temperature has two effects on drying. First, increasing temperature of the air causes a corresponding decrease in the relative humidity of the air, which increases the driving force for moisture loss. Second, the higher temperature means faster diffusion of water molecules from the wet layer into the drying air. Because of the two-pronged effect, increasing air temperature is probably the most effective means to speed the rate of drying, although drying air temperature (like engrossing syrup temperature at application) must remain below the point where the center becomes too soft or melts. The relative humidity of the drying air can also be reduced to enhance drying since this increases the driving force for moisture loss (from syrup to air). However, reducing relative humidity too low (below 20%) causes such rapid drying that the glassy state is formed, inhibiting further crystallization. Proper choice of drying air parameters is required to enhance application of the hard-panned shell and increase the efficiency of operation.

One of the primary concerns in traditional batch hard panning is reducing cycle time to reduce total batch time. If only drying was of concern, a logical approach would be to speed drying by applying hotter and dryer air at a higher circulation rate in the pan. However, the end result of this approach would be to delay crystallization, which would lead to quality problems later. Such rapid drying would essentially trap moisture within the shell in the form of a glassy state and prevent proper crystallization. When that water was released by subsequent crystallization, it would take any soluble dyes with it, which would result in an uneven, mottled appearance.

Further details on the competitive processes of drying and crystallization from thin sugar syrup layers can be found in Shastry and Hartel (1996) and Ben-Yoseph and Hartel (1999).

13.4.2 Moisture Migration

As with most confections, controlling water content during sugar panning, both during processing and storage, is critical to controlling product texture, quality and shelf life. Since relatively high moisture content engrossing syrup is applied to the centers tumbling in a pan, it makes sense that moisture changes during processing are important to setting the proper structure of both hard and soft-panned candy shells.

13.4.2.1 Soft-Panned Candies

In soft panning, engrossing syrup with 75–78% dissolved solids content (22–25% water) is applied to a center with varying water content. Jelly centers, probably the most common center for soft panned candies, typically contain water content of 8–15%. Even though the higher water content engrossing syrup is quickly packed with dried powder, this difference in water content (and chemical potential) leads to moisture migration between engrossing syrup and center. To allow for moisture migration and the subsequent crystallization of the shell to attain phase equilibration, many soft-panned candies are held for a time of curing (or stoving) before polishes are applied to the shell surface.

In practice, moisture migration during aging of soft-panned jelly beans is more complex than simple equilibration between shell and center since water within the confection must also equilibrate with the surrounding air (Troutman et al. 2001). As noted in Chapter 3, the parameter that drives moisture migration between two zones (either different regions of a candy or between the candy and the surrounding environment) is not water content, but the chemical potential of water molecules in the two different regions. That is, water activity of the two regions (or more accurately, water vapor pressure) determines which way moisture migrates and when moisture migration will stop.

In the Troutman et al. (2001) study of water migration during aging of starch-based jelly beans, the initial (immediately after panning) water content of the shell was between 4% and 4.5% whereas the jelly bean center had a water content of about 8%. If it was water content that drove migration, water would move from center to shell. However, the initial water activity (ratio of vapor pressures) of the shell was about 0.75–0.76 while that of the jelly center was between 0.60 and 0.65. Thus, moisture migrated initially from the shell to the center. The differences in water activity between shell and center are due to the different sugar composition and the effects of those ingredients on water activity (see Chapter 3 for more details). Different centers (pectin, gelatin, or mixtures of hydrocolloids) may not behave the same way as the starch-based centers in this study.

During aging, moisture initially migrates from shell to center in order to attain a water activity equilibrium – moisture would continue to migrate until the water activities of the two regions were the same. However, a second driving force for moisture migration exists during stoving that alters this balance. Water must also equilibrate between the candy and the surrounding air. In the case of the Troutman et al. (2001) study, the air conditions in the aging room were 21.1 °C (70 °F) and 70 ± 5% relative humidity, typical curing conditions for many operations. The initial water activity (vapor pressure) of the sugar shell was higher than the relative humidity (vapor pressure) of the surrounding air. Thus, in addition to water migration from shell to jelly center, there was also a driving force for water to migrate from the sugar shell into the aging-room air. Water in the shell was driven in two directions, into the jelly center and into the air, resulting in a complex dynamic state that resulted in substantial changes in the jelly bean. After 2 days at curing conditions, moisture had redistributed within the jelly bean. The jelly center had a water content of 6.5–7.0% and a water activity of 0.60–0.62, whereas the sugar shell had water content of 3.4–4.0% and water activity of about 0.68. The entire jelly bean had lost about 0.3% of its initial weight due to moisture loss to the air. And, drying was still occurring even after 2 days, since the jelly bean had not yet equilibrated with either itself (shell to jelly center) or with the surrounding air.

For various reasons (efficient operations and enhanced throughput, etc.), moisture migration during curing is probably never completely attained before the polish layer is applied. Since the polish/glaze layer is usually a good (although not complete) moisture barrier, once the polish is applied, moisture migration to the surrounding air slows dramatically, allowing moisture migration within the candy piece to occur. If the polish/glaze layer is applied before sufficient curing has been allowed, the trapped moisture can potentially cause shelf life problems as it slowly equilibrates during storage. In particular, excessive moisture migration after polishing and glazing leads to problems like sticking and caking of soft-panned goods within the package. A bag of fused jelly beans is generally caused by lack of control of moisture during panning.

Furthermore, since the polish/glaze layer is not a complete water barrier, moisture migration still occurs between the soft-panned candy and the surrounding air. This moisture loss, and the hardening of the candy that accompanies it, is one of the primary modes of product failure in shelf life (see Section 13.4.3).

13.4.2.2 Hard-Panned Candies

The moisture migration that occurs both during and after completion of panning is also important to the quality and shelf life of hard-panned candies. As any experienced pan operator knows, the shell of a freshly-made hard-panned candy has a significantly softer texture than the finished product after moisture equilibration. Despite the drying step in each syrup application cycle, the shell does not complete crystallize during the panning operation nor has it reached its final moisture level. In the same way as soft-panned candies, over time, the water within the shell migrates to reach equilibrium with the center and the surrounding air. Due to the nature of hard-panned centers, however, moisture migration into the candy center may be significantly less important than in soft-panned candies. In particular, chocolate and nut centers take up very little moisture from the sugar shell.

The engrossing syrup in hard panning generally contains up to about 30% moisture (lower for engrossing but higher for smoothing) when it is applied to the tumbling centers in the pan. Since the final water content of the sugar shell is close to 1–1.5% (water activity of 0.3–0.35), almost all of the water applied in the engrossing syrup must be driven off to reach the desired shell conditions. Much of that water is evaporated during the drying cycle, but not all of it. Although no quantitative data have been published on water content at different locations and times during hard panning, it is likely that the water content of the shell is still 3–4%, or higher, at the point when the operator decides another layer should be applied. This water remaining in the shell during panning must diffuse out to the air as equilibration between the sugar shell and the air occurs. If too much moisture remains within the shell, this moisture may carry soluble dyes as it migrates out, leaving the candy surface with a mottled and disfigured appearance. Lake-based colors are often used in hard panned shells to prevent this problem.

Aggressive drying cycles, often used when cycle times must be shortened to enhance product throughput, can cause additional moisture migration problems. When extreme drying conditions (high air flowrates, warm temperatures, and low humidity) are used, each applied layer is likely to contain excess water as the layer approaches the glassy state (Figure 13.14). When the surface becomes glassy, the operator may consider the surface sufficiently dry to warrant the next engrossing syrup application. However, the excess water and incomplete crystallization can lead to moisture migration problems later as the shell goes through the equilibration process.

Moisture migration is also influenced by the continuation of sugar crystallization over time, which further enhances moisture mobility. When sugar crystallizes, the concentration of sugar molecules in the liquid phase decreases (desupersaturation), which allows water molecules greater mobility to migrate through the shell. Thus, both sugar crystallization and moisture loss occur for some time after the candy pieces have been removed from the pan. Adequate time is needed for these processes to be completed before polishing. If the polish layers are applied immediately after panning is completed, before moisture has had a chance to equilibrate, what looks initially like well-polished product quickly becomes dull as moisture interacts with the polish layers. Although waxes and glazes provide some water barrier properties, neither is a complete barrier to moisture. Equilibration with the air occurs even through the polish layers, just more slowly.

In hard-panned candies where the sugar shell and center have different water activities, moisture migration occurs during storage and often leads to the end of shelf life of the product. This will be covered in the next section on shelf life of sugar-panned candies.

13.4.3 Shelf Life

Well-made sugar panned candies can have a shelf life over a year given proper storage conditions. The combination of a tight sugar shell and the polish/glaze layers provides protection against most deteriorative processes. Probably the main mode of deterioration of soft-panned candies is moisture exchange with the environment, most often leading to drying out and hardening of the center. Hard-panned candies are also prone to moisture migration issues if the center has higher water activity than the shell. Other changes (flavor loss, lipid oxidation, etc.) may occur in certain hard-panned confections.

13.4.3.1 Soft-Panned Candies

Soft-panned candies are prone to moisture changes depending on the conditions of storage. With water activities of 0.6 or higher, soft-panned candies like jelly beans and fruit sours are subject to drying out if stored in conditions where relative humidity is lower than about 50%. It is quite common for even a sealed bag of soft-panned candies to get harder over time as moisture is lost to the air. Most candy wrappers are not perfect moisture barriers so that gradual moisture migration through the package occurs during shelf life. As moisture is lost from the candy to the air, the texture of the candy changes. Lower moisture content means harder candy, so soft-panned candies typically toughen during storage until the point where the consumer considers the candy too hard to eat. Use of packaging material with higher moisture barrier properties would allow shelf life to be extended, but the cost of the improved packaging material is often not worth the extension of shelf life.

When stored in excessively high temperatures (35–40 °C; 95–104 °F) and humidity (in excess of 75% RH), soft-panned candies can absorb moisture from the air. Although a good polish/glaze layer provides some level of water barrier properties, over time the moisture can migrate into the shell and cause softening and stickiness. Candy pieces in contact within a bag may then stick together, and when conditions change at a later time (temperature and humidity decrease), the points of contact can cause fusion of candies together. What was initially a bag of free-flowing candies can become a hard lump of candy if exposed to high temperature and humidity for too long a time. Moisture pick up can also lead to running of colors as dye molecules migrate with the water molecules.

Ideal storage conditions for soft-panned candies to minimize moisture migration would be slightly cool temperatures (room temperature or slightly lower) and moderate humidity of about 50–55%.

13.4.3.2 Hard-Panned Candies

Moisture migration is also often an issue for shelf life of hard-panned candies, particularly in those with a water-based center. For example, hard-panned gum centers go through an equilibration process during storage since the gum center typically has higher water activity (0.45–0.5; about 2% moisture content) than the hard-panned sugar shell (water activity of about 0.3 and about 1% moisture content). Over time, moisture from the gum center migrates into the sugar shell as the two tend toward the same water activity, causing the gum to become too firm while at the same time softening the shell. However, external storage conditions can substantially impact moisture migration and shelf life since the candy must also equilibrate with the environment.

Despite the water barrier properties of packaging materials and polish layers, moisture migration between a hard-panned sugar shell and the ambient air also occurs. These barriers slow down the rate of moisture migration, but over long terms of storage, ambient conditions can have significant effect on certain types of hard-panned confections. In principle, an ambient relative humidity above 30% can lead to moisture migration from the air into the hard-panned sugar shell (water activity of about 0.3); however, the rate of migration through the packaging and polish barriers is minimal until ambient relative humidity substantially higher, perhaps as high as 70%. Higher relative humidity of course leads to faster moisture migration.

When exposed to air with relative humidity of 75%, a hard-panned sugar shell can rapidly pick up moisture and soften over time. The crisp bite of the sugar shell is lost as moisture content increases, with the softening due in part to dissolution of sugar crystals, which also dissolves away the inter-crystal bridging of the network of small crystals that give the hard bite. Any moisture migration from the center (as in the gum example) adds to the rate of moisture change and softening of the sugar shell. At the same time, the overall appearance of the candy will change as the polish layer becomes dull and soluble dyes migrate within the shell.

Ideal storage conditions for hard-panned candies are cool (16–20 °C; 60–68 °F) and dry (RH <50%). The low temperatures reduce the rate of moisture migration and low humidity minimizes potential moisture pick up from the air.

13.5 Troubleshooting

Sugar panning is one of the most difficult candy-making practices. Becoming an accomplished panner requires extensive training and practice since there are numerous ways to make mistakes. One trait of primary importance for proper panning is patience. Kitt (1988) provides an excellent summary of panning problems and their remedies.

There are a vast number of parameters that must be controlled during panning and this is, in part, what makes sugar panning one of the most difficult confectionery practices. The parameters that affect panning may roughly be broken down into those that affect the pan or tumbling candy, those that affect the engrossing syrup or the process of syrup application, or those parameters that affect polishing and glazing. Table 13.2 summarizes these parameters.

13.5.1 Soft-Panned Candies

For the novice panner, formation of doubles or clumping is often the most vexing obstacle to making good soft-panned product. Typically, clumping is most often caused either by the addition of too much engrossing syrup prior to addition of the dry powder charge or by addition of engrossing syrup that is too viscous (either too concentrated and/or too cold). Alternatively, engrossing syrup that is too hot can cause double formation from excessive softening of previous layers. Also, centers that were not properly precoated, slow pan speed and delayed addition of the dry powder charge can lead to formation of doubles. Finally, centers with a large flat surface are difficult to pan without forming doubles since it is highly favorable for the flat surfaces of two adjacent pieces to stick together.

A soft or even collapsed shell can be caused by several problems. Soft shells are often due to improper engrossing syrup formulation. Engrossing syrup that is too viscous, improperly formulated (corn syrup ratio too high) or has too much inversion can lead to a soft shell. Collapsed or distorted shells may also be caused by improperly formulated engrossing syrup but is more often attributed to excessive contact forces as the pieces tumble in the pan. Either the candy falls too far onto the bed as it tumbles, bed depth is too high or the pan speed is too high. Very soft or flexible centers are also prone to distortion of the sugar shell, with the tumbling forces causing deformation of the center resulting in excess flexing of the shell.

Rough or uneven surfaces can be caused by numerous factors, generally related either to the engrossing syrup or the dry powder charge. One of the most obvious causes of rough surfaces is that the engrossing syrup does not sufficiently coat the centers. An insufficient amount of engrossing syrup to completely coat the surface may cause rough surface, but addition of too much engrossing syrup may also cause an uneven surface because of the excess amount of dry powder that needs to be added. The engrossing syrup also may be too viscous to coat the surfaces, particularly if it is too cold or at too high a concentration. Rough/uneven surfaces may also be due to improper dry powder charge addition. If too little or too coarse a powder is added, the surface will not reach the desired smoothness. Too much addition of dry sugar can also lead to a rough or lumpy surface since the excess powder collects in the pan, to be picked up with the next charge of engrossing syrup. Finally, a pan rotating too slowly for the nature of the centers may not generate enough collision forces to smooth out the sugar layers, leading to a rough surface.

The texture of a soft-panned sugar shell can vary from very soft to excessively hard depending on the nature of the sugar crystals. Typically, hard shells are caused by excessive crystallization and subsequent bridging as the engrossing syrup equilibrates with the powder charge. Engrossing syrup that is applied at elevated temperature, or has either high sucrose level or water content can lead to excessive crystallization and bridging. Application of drying air during soft panning would also lead to reduced water content, excess crystallization and harder shell. Other potential causes for hard shells may be excessive dust or fines in the pan, use of a sugar granulation that is too small, or too much engrossing syrup addition.

Although typically more a problem with hard panned sugar shells, color mottling may also be a problem in soft-panned candies. Improper dry charge addition may result in excess moisture remaining in shell layers, and later as moisture equilibrates, any soluble dyes will migrate with the water, leading to an uneven color distribution. In certain types of centers with high oil content (e.g., Boston baked beans), oil migration from center to shell can also cause changes in color dispersion. Use of a pre-coat material to seal the centers may be necessary to resolve oil migration issues.

13.5.2 Hard-Panned Candies

Although not as significant a problem as for soft panning, formation of doubles and multiple clumps of centers can also occur in hard panning, and for mostly the same reasons. When more engrossing syrup is added than needed to just coat the centers, the surface becomes excessively sticky and the candies stick together. Clumping may also be due to using engrossing syrup that is too viscous, whether because of high concentration or low temperature. Center shape plays a huge role in double formation in hard panning, with flat-sided centers being most prone to clumping. Finally, sufficient tumbling action is needed to ensure that there are sufficient forces to break up any clumps.

Rough surfaces in hard-panned candies are a common problem, one that can be caused by a number of factors. First, if the center has a rough surface, typically the sugar shell will also be prone to unevenness. Rough-surfaced centers should be adequately precoated to smooth out unevenness to give smooth panned shells. Rough surfaces can also be caused by improper application of engrossing syrup and subsequent drying of the layer. A rough surface can result if the engrossing syrup concentration is too high, if either too much or too little of the engrossing syrup is added or if the applied syrup layer is dried too rapidly (air too fast and/or too hot). Excessive dusting, caused by allowing the product to tumble too long after it has been adequately dried, can also lead to rough surfaces. Factors that cause a rough surface can also lead to formation of holes in the coating. Sucrose-based shells are particularly prone to rough finishes if the engrossing syrup has accidentally grained. When sucrose crystal seeds are applied with the engrossing syrup to the sugar shell, these seed crystals grow to excessively large size during drying and disrupt the microstructure of the shell. Interestingly, if seed crystals are present during dextrose hard panning, the same problem is not observed. Probably the naturally small size of dextrose crystals allows completion of the shell without marring the desired crystalline microstructure.

Cracks that form in the hard-panned sugar shell are often an important concern for candy makers. Any flexing or softening of the center, particularly as temperature changes, can put stress on the sugar shell that can eventually lead to cracking. Controlling and minimizing temperature fluctuations can help alleviate the problem, but pan operators often add low levels (≈1%) of materials like glucose syrup gum arabic or maltodextrin to make a more pliable shell that is better resistant to cracking. Chipping of the sugar shell is also a potential problem, particularly when there are sharp edges and a thin shell is desired. Again, low levels of additives can make the shell more pliable, but reducing tumbling forces can also help minimize chipping.

Another important concern of the hard-panned candy maker is uneven or mottled color. This can be caused by a rough surface, where the color layers take slightly different thickness and impart slightly different hues. However, the problem may also be traced either moisture or oil migration. If the sugar shell is dried too quickly (for example, to reduce cycle time), excess moisture remains within each layer of the shell as the next layer is applied. Over time, each layer of the shell must equilibrate in water content, particularly if additional crystallization occurs over time. When the excess moisture moves to the surface to equilibrate with the environment, it can carry soluble dyes along with it and cause an uneven distribution of the color. Rearrangement of color due to moisture migration is minimized with use of lakes.

If the sugar shell takes an unreasonably long time to dry and/or has a tacky surface, it is most likely caused by impurities in the engrossing syrup that inhibit crystallization. In sugar shells, it is most likely caused by inversion of the sucrose from being held at high temperatures too long prior to use. Acid conditions make inversion worse. In some cases, color dispersions may also impact sugar crystallization.

13.5.3 Polishing and Glazing

A well-polished panned candy is attractive and appealing to the consumer. On the other hand, a poorly polished candy detracts from consumer appeal and negatively affects sales. A dull finish on a polished candy can be caused by any one of several potential problems.

One important consideration in applying a polish or glaze is moisture, both within the shell and in the environment during polishing. It is imperative to make sure the candies have been properly dried and equilibrated after panning has been completed prior to applying a polish or glaze. Often, 1–2 days of curing are needed for soft-panned candies to ensure adequate moisture equilibration. Hard-panned candies can be polished after only a brief period of drying. If panned candies are polished immediately after completion of panning, the migration of water between shell and air causes the polish layer to become dull. As the water molecules slowly diffuse through the polish layer to equilibrate with the air, they disrupt the glaze surface, leading to a dull surface. Polishing is also difficult to perfect when the air in the polish room is too humid. Again, water molecules disrupt the polish layer and make it impossible to attain the desired appearance.

Another enemy of a well-polished panned candy is dust or any other particulate matter on the candy surface. Whether from over-drying or inadequate removal of removal of powdered sugar, the presence of particles on the shell surface disrupts the ability to spread the polish or glaze on the surface. Typically, sugar shells are finished with a low concentration (65%) engrossing syrup to smooth the surface and remove dust and other sugar particles.

Finally, incorrect application of the polish can be cause of a dull surface appearance. Wax layers are particularly sensitive to application levels. If too much wax is applied, it will not develop a satisfactory shine. Wax levels should be about 0.05–0.1% of the batch weight.

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Chewing and Bubble Gum

14

14.1 Introduction

Over the years, man has chewed various things for health and pleasure. In ancient Greece, people chewed resin of the mastic tree. This mastiche, as the product was called, was thought to help clean teeth and freshen breath. In the Americas, the native North Americans chewed tree sap and the Mayan Indians chewed chicle, the sap (or latex) from the sapodilla tree, which grows in Central America. This predilection of early man for putting things in the mouth and chewing it has led to the one of the largest categories of confectionery products – gum.

Although man has chewed various things for millennia, the first chewing gum in the United States was not manufactured until the late 1840s with the development of the State of Maine Spruce Gum. The first US patents on chewing gum were issued in 1869, although the history of chewing gum was already well-developed by then, based on the title of Semple's patent – Improved Chewing Gum. Despite these earlier developments, many consider the birth of modern gum to be when chicle was brought to New York by General Santa Anna of Mexico in 1869. Experimentation with Santa Anna's chicle by Thomas Adams led to commercialization of chewing gum.

People chew gum for many reasons, which may loosely be broken down into medical and psychological reasons (Table 14.1). Leveille et al. (2008) cite research that supports the following benefits of chewing gum: (1) saliva and oral health, (2) stress relief, (3) improved cognitive performance, and (4) weight management. Whether for the sweet enjoyment or for health reasons, chewing gum is a popular activity with sales in the United States exceeding three billion dollars each year.

Gum comes in many different forms and types, from sticks to gum balls. Gum also comes in powder form and there is even a liquid gum (or paste) available in a tube. Gum may be designated as either chewing or bubble gum. Regardless of the form, however, the ingredients are essentially the same. Gum base, made from either natural or synthetic polymers, is the main ingredient. Various chemical modifiers may be added to the gum base to provide specific functionality (i.e., softening, reduced stickiness, longer lasting flavor, etc.). Slight differences in the gum base, particularly the nature of the higher molecular weight polymers, provide the difference in the ability to form a bubble. A bulk sweetener, whether sugar or sugar alcohol (sugar free), provides bulk, texture and sweetness to the gum. Humectants (glycerol, liquid sorbitol, HSH, etc.) may be added to control moisture loss during storage and antioxidants added to limit oxidation. Colors and flavors are generally added to provide a unique eating experience and organic acids may be added to complement certain types (e.g., fruit) of flavors. Gum typically has very low water content, between 3.5% and 5%.

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Table 14.1 Potential reasons why people chew gum

Medical reasons:
Freshens the mouth and breath
Cleans the teeth
Aid to digestion
Soothes the throat
Stimulates saliva production (reduces dry mouth, xerostomia)
To deliver some active agent (i.e., nicotine, caffeine, etc.)
Psychological reasons:
Enhances relaxation
Relieves nervous tension
Calms anger
Steadies the nerves
Invites happiness
Attracts smiles
Fun and enjoyment (e.g., blowing bubbles)
Sweet treat
Others:
Relieves air pressure on ear drums
Strengthens the jaws

To produce gum, the ingredients are first mixed together until they are blended thoroughly. Mixing is most often done in a batch mixer with a high-torque motor, although continuous extrusion processes are becoming more common. After the ingredients are fully mixed together, the warm gum mixture is usually cooled slightly to control firmness prior to forming gum pieces in an extruder. The extruder output is usually either a slab or sheet of gum or a rope (hollow or solid). Further sizing operations may be needed to bring the gum to the correct thickness and/or shape. After additional cooling to attain the desired firmness, the gum is either cut into the desired sizes (slab or stick) or formed (hollow ball) into the desired shape. Numerous shapes are available with modern extrusion and forming equipment. Additional cooling is often necessary to allow the gum mass to solidify sufficiently that it can be wrapped. This may be done in a cooling tunnel or by holding overnight in storage rooms prior to packing the next day. Many types of gum (dragees, gum balls, etc.) may be hard-panned to provide a crunchy coating (see Chapter 13 for more on hard sugar panning).

Gum is a complex multi-phase material, with each component playing a unique role in determining gum properties and shelf life. Microstructurally, gum is a dispersion of particles (sugar, etc.) in a mostly amorphous matrix (gum base) with a minor amount of aqueous sugar syrup distributed throughout. The dispersed powder phase makes up over 60–70% of the gum piece with the amorphous phase (gum base, humectant, liquid sweetener, etc.) comprising about 30–40%. Gum base is not entirely amorphous since some of the fats and waxes crystallize within the gum base during solidification.

The eating properties of gum are dependent on the microstructure as well as the characteristics of the ingredients added. There is a rapid initial release of flavor and sweetness as the sweetener dissolves when the gum is first chewed. At the same time, the gum base hydrates and swells. Typically, the flavor and sweetness of the gum lasts for a short time (3–10 min), leaving the perception of an essentially flavorless cud (or bolus) of moistened gum base. Deeper analysis, however, shows that over half of the initial flavor load remains trapped due to the solubility of flavors in the gum base; many flavor molecules are lipophilic and prefer gum base (a hydrophobic material) to saliva (an aqueous material). Gum companies work hard to deliver longer-lasting flavor and sweetness through continually improving both manufacturing technologies and ingredient capabilities. Another important attribute for certain types of gum is the ability to form and hold a bubble. Whether or not a gum has the ability to retain bubbles is determined by the nature of the polymers used in the gum base. Typically, higher molecular weight polymers (which are plasticized in the gum) are used to provide the elastic properties necessary for creating bubbles. Lower molecular weight polymers tend to break too easily as they are stretched, giving limited bubble formation ability.

The shelf life of a gum is primarily dependent on moisture loss or gain, although flavor loss can sometimes be a concern. The change in moisture content during storage can cause gum to either get hard and firm (moisture loss) or become sticky (moisture gain). Since the water activity of gum is generally between 0.5 and 0.6, storage at relative humidity values less than 50% cause moisture loss, whereas storage at RH greater than 60% cause moisture gain and stickiness.

Chewing gum has been around for over a hundred years and makes up one of the largest segments of the confectionery industry. Despite this, the science and technology that go into the manufacture and storage of gum are often still not very well understood. Gum companies are also highly secretive, keeping their developments either within house or protected by patents.

14.2 Formulations and Ingredients

Chewing gum is made by mixing a gum base with other ingredients, including sweeteners, flavors, colors, organic acids, and humectants. An "active" ingredient may be added for functional purposes. Sugar-free gums typically contain sugar alcohols to replace the bulk sweeteners and may also have a high-intensity sweetener to enhance sweetness. The general ranges for ingredient addition in gum are given in Table 14.2. Although the range of formulations varies widely with gum manufacturer, some general trends are seen in ingredient composition. Since the amount of gum base primarily determines cud size, smaller gum pieces (pellets, tabs, etc.) typically contain higher (25–30%) levels of gum base, whereas larger pieces (sticks, etc.) contain lower (20–25%) levels. Gum pieces that need to withstand the forces during tumbling in pan-coating typically have higher levels of fillers and/or lower levels of glucose syrup to increase firmness.

Table 14.2 Typical ranges of components of chewing gum

Ingredient	Content (%)
Gum base	17–30
Mineral filler	<10
Bulk sweetener	70–85
Softener	1–6
Acid	0–2
Flavor	0.75–3
High intensity sweetener	0.005–1
Color	
Dye	≈0.03
Lake	0.1–0.3

The cost and quality of gum is governed by the choice of ingredients. For example, the amount and nature of the gum base polymer (e.g., molecular weight distribution of rubbers and other polymers) used determines such properties as the chewing characteristics, mouth feel, and the ability to blow bubbles. The level and type of texturizers used in gum are critical to cost and quality, with higher levels of fillers giving less expensive, but lower quality, gum. Of the many reasons for chewing gum, flavor is one of the most important attributes for the consumer. Thus, the amount of flavor and its release profile are of considerable importance to the gum maker. It is critical to understand flavor interactions with gum base in order to produce a gum with the desired texture and flavor release.

14.2.1 Gum Base

The main ingredient in gum is the gum base, which gives the characteristic chewy nature. Gum base, the component that holds the entire piece together, provides desirable chewing characteristics (neither too soft or too hard) and proper release of sweeteners and flavors. Gum base is a mixture of plasticized rubber polymers, either natural or synthetic, often with other functional ingredients to provide certain characteristics. The polymers do not dissolve in the mouth, thereby providing a long lasting chew. To the polymer matrix, various softening agents, fillers and texturizers, oils and emulsifiers, and antioxidants may be added. Gum base is one of the most secretive ingredients in all of confections, with companies carefully protecting their specific formulations and knowledge base.

Gum base has a Standard of Identity, as defined in the Code of Federal Regulations (US FDA 21CFR172.615). It is "A food additive consisting of one or more of the following substances that meet the specifications and limitations prescribed in the paragraph and used in amounts not

Table 14.3 Ingredients allowed in chewing gum base (from US FDA 21CFR172.615)

Natural gums (natural rubber – polyisoprene):	
	Coagulated or concentrated lattices from various plant sources
	Sapotaceae (includes chicle), Apocynaceae, Moraceae, Euphorbiaceae
Synthetic polymers:	
	Butadiene-styrene rubber
	Isobutylene-isoprene copolymer (butyl rubber)
	Polyvinyl acetate
	Paraffins
	Petroleum wax, petroleum wax synthetic, polyethylene, polyisobutylene
Plasticizing materials (softeners):	
	Glycerol esters (of various rosins)
	Lanolin
	Methyl ester of rosin (partially hydrogenated)
	Pentaerythritol ester of partially hydrogenated gum or wood rosin
	Pentaerythritol ester of gum or wood rosin
	Rice bran wax
	Stearic acid
	Sodium and potassium stearates
Terpene resins:	
	Synthetic resin (polymers of α-pinene, β-pinene, and/or dipentene)
	Natural resin (polymers of α-pinene)
Antioxidants:	
	Butylated hydroxyanisole (BHA)
	Butylated hydroxytoluene (BHT)
	Propyl gallate
Miscellaneous:	
	Sodium sulfate
	Sodium sulfide
Texturizers (allowed under the category of other GRAS additives):	
	Talc (food grade)
	Calcium carbonate
	Dicalcium phosphate
Others:	
	Hydrogenated vegetable oils
	Lecithin, mono- and diglycerides

to exceed those required to produce the intended physical or other technical effect.” Table 14.3 summarizes the allowed ingredients in chewing gum base, although as stated at the end of the regulations, any other substance with GRAS (generally recognized as safe) status may also be added to gum base. Texturizers, used to aid processing and to modify mouth feel, are typically mineral adjuncts like talc and calcium carbonate. Other texturizers, or fillers as they are often called, include cellulose fibers and organic fibers.

The original chewing gums were made from natural rubbers, like that exuded from the chicle tree of Central America. Chicle contains approximately 60% of resin and 15% of rubber. The resin consists of lupeol, α-amyrin and β-amyrin, and the rubber fraction contains *cis*- and *trans*-1, 4-polyisoprene (Misawa 1994). Different impurities provide differences among the natural rubber tree species. For a variety of reasons (cost, availability, and consistency), natural rubbers are now rarely used in chewing gum, having been replaced by synthetic polymers. The primary components of modern gum are the food-grade synthetic rubber polymers, particularly butyl rubber (IIR), styrene-butadiene rubber (SBR) and polyisobutylene (PIB), shown structurally in Figure 14.1. Butyl rubber, also known as isoprene-isobutylene copolymer or rubber; IIR) is a polymer made up primarily of isobutylene units with small amounts (2–4%) of isoprene polymerized with the isobutylene. Lower molecular weight polymers are also typically added to gum base to impart specific properties. These include synthetic polymers such as polyvinyl acetate (PVAc), which imparts a less elastic, more plastic texture to gum base, and vinylacetate-vinyl laurate copolymers.

Both natural and synthetic rubber polymers used in gum exhibit elastic properties, depending on the chemical make-up and molecular weight of the polymer. The nature of the gum product can be significantly influenced by the composition of the gum base. Choice of gum polymer and additives provide the difference between chewing and bubble gum, impact textural properties (i.e., hardness, elasticity/bounciness, stickiness, bubble capacity, etc.) of the gum, and influence the cost. The acid resistance of a gum base is also dependent on the texturizers used. In general, higher quality gum base contains more rubber and less of the inexpensive texturizer components. High quality chewing gum base contains 5–20% texturizers, whereas in more economical gum base, these levels can be as high as 50–55%. Higher

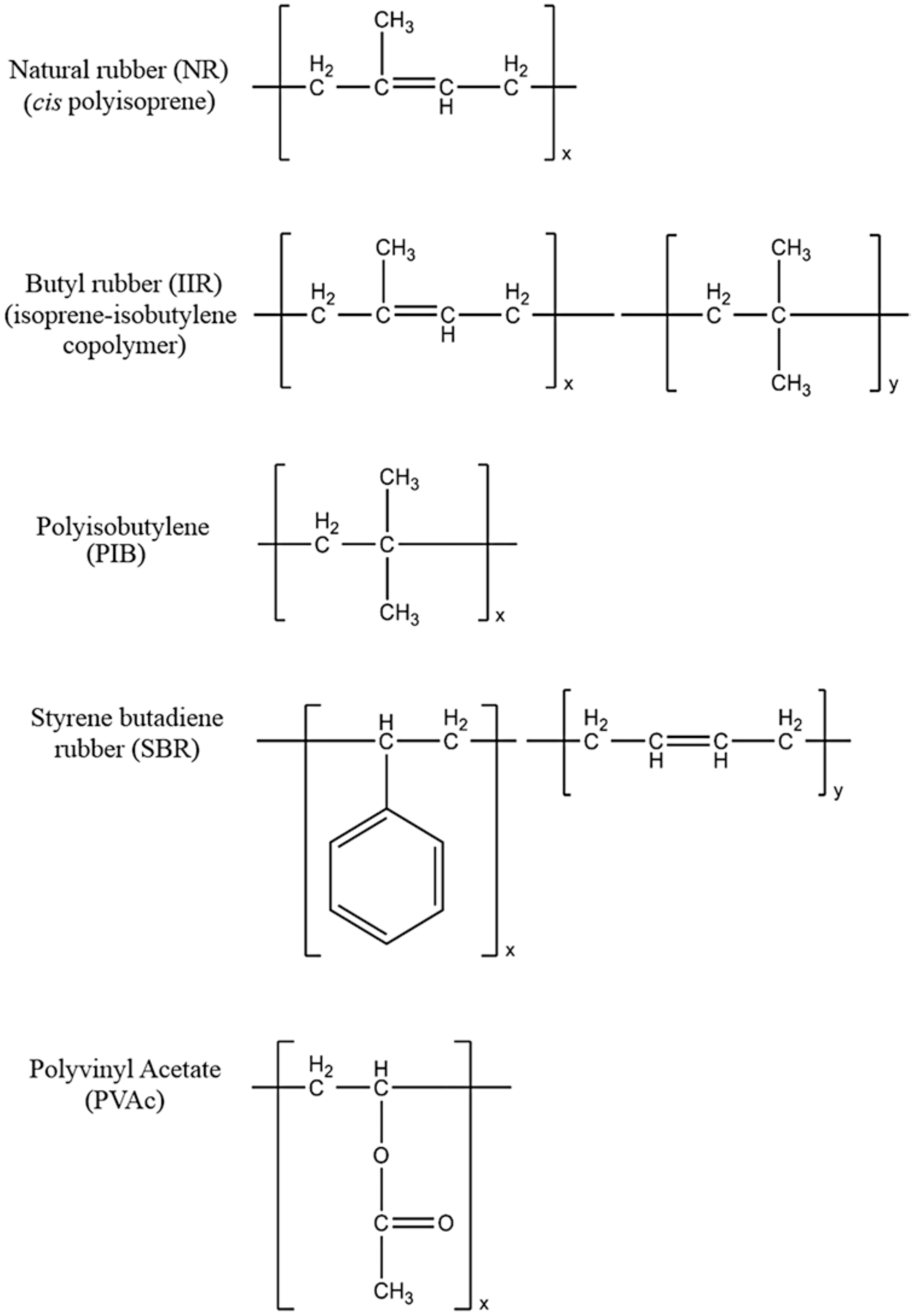

Figure 14.1 Chemical structures of synthetic polymers used in gum base

levels of texturizers reduce stretch in the gum and alter the size of the cud left after chewing.

The main differences between chewing gum and bubble gum relate to the composition of the gum base. To sustain bubble formation, bubble gum contains higher levels of rubber, and typically higher molecular weight rubbers (polymers), than in chewing gum. Bubble gum contains from 30% to 60% texturizers according to the desired quality (higher quality generally means lower level of texturizers).

To make gum base compatible with acids, as used in fruit flavors for example, food grade talc is usually used as texturizer instead of calcium carbonate. The well-known acid-base reaction between calcium carbonate and organic acids leads to instability of the gum over time and loss of acidification for flavor enhancement. Thus, calcium carbonate must be replaced with a material that does not react with the acid.

Various additives have been evaluated in gum base to provide specific characteristics, such as reduced stickiness and enhanced biodegradability. For example, proteins, polypeptides and degradable polyester polymers from cyclic esters (lactides, glycilactides, etc.) have been suggested for use in gum base to enhance environmental breakdown. Numerous patents have been issued on these topics.

Since gum base is prone to oxidation, antioxidants are sometimes added to extend shelf life. Common antioxidants include butylhydroxytoluene (BHT), butylhydroxyanisole (BHA) and tocopherol (Vitamin E).

Although sometimes not considered part of the gum base, other softeners or plasticizers may be added to a gum formulation to provide specific physical properties through their interaction with the gum base. Oil-based materials like lecithin (0.1–0.3%), hydrogenated or fractionated vegetable oils (0.1–0.2%), and triacetin (0.1–0.3%), for example, may be used to soften the gum base. Certain types of flavors (e.g., essential oils) can interact with the gum base to moderate chewing properties, and their effect on overall gum quality must be considered in the formulation.

Gum base is made by sequentially adding each of the ingredients into mixers with high power motors. An example of a continuous gum mixing device is shown in Figure 14.2. Temperature must be sufficiently high to soften all ingredients and shear forces must be intense enough to completely homogenize the mass. The warm, well-mixed gum base may be used directly in liquid form to be added to a chewing or bubble gum formulation or it may be formed and cooled for subsequent transport to a gum manufacturer. Solidified gum base is found in a variety of forms, including 10 kg blocks, sheets, pellets, or tablets.

14.2.2 Sweeteners

Numerous sweeteners have been used in chewing gum. Sugars (sucrose or dextrose) and glucose syrup are most common in sugar-based gum. Sugar alcohols like sorbitol, mannitol, xylitol, maltitol and isomalt along with hydrogenated starch hydrolysates (HSH) are used for sugar-free gums. In addition to sweetening, these ingredients also provide bulk/body to the gum, influence flavor release and shelf life, and may provide a cooling effect as they dissolve (heat of solution). Certain polyols, in particular, have a very large heat of solution and cause a significant cooling effect (Section 2.3).

14.2.2.1 Sucrose

In sugar-based gum, finely ground refined sugar powder is uniformly mixed into warmed gum base in a powerful mixer to give a final sucrose content of over 50%. Probably the most important parameter for the sucrose powder, other than that it is of high purity, is the particle size. It is generally undesirable that individual sugar crystals be detected in the mouth during chewing of gum and thus, the particle size must be less than the threshold detection value in a gum matrix. To ensure a smooth mouth feel, 96% of the sugar powder should pass through a 200 mesh screen, meaning that the majority of particles are smaller than 74 μm. Some say that a particle size of 45 μm is ideal for gum.

The size of sugar crystals and the amount of sugar powder in gum also affects texture. In general, the higher the crystal content in a gum, the firmer the piece will be. Also, smaller sugar

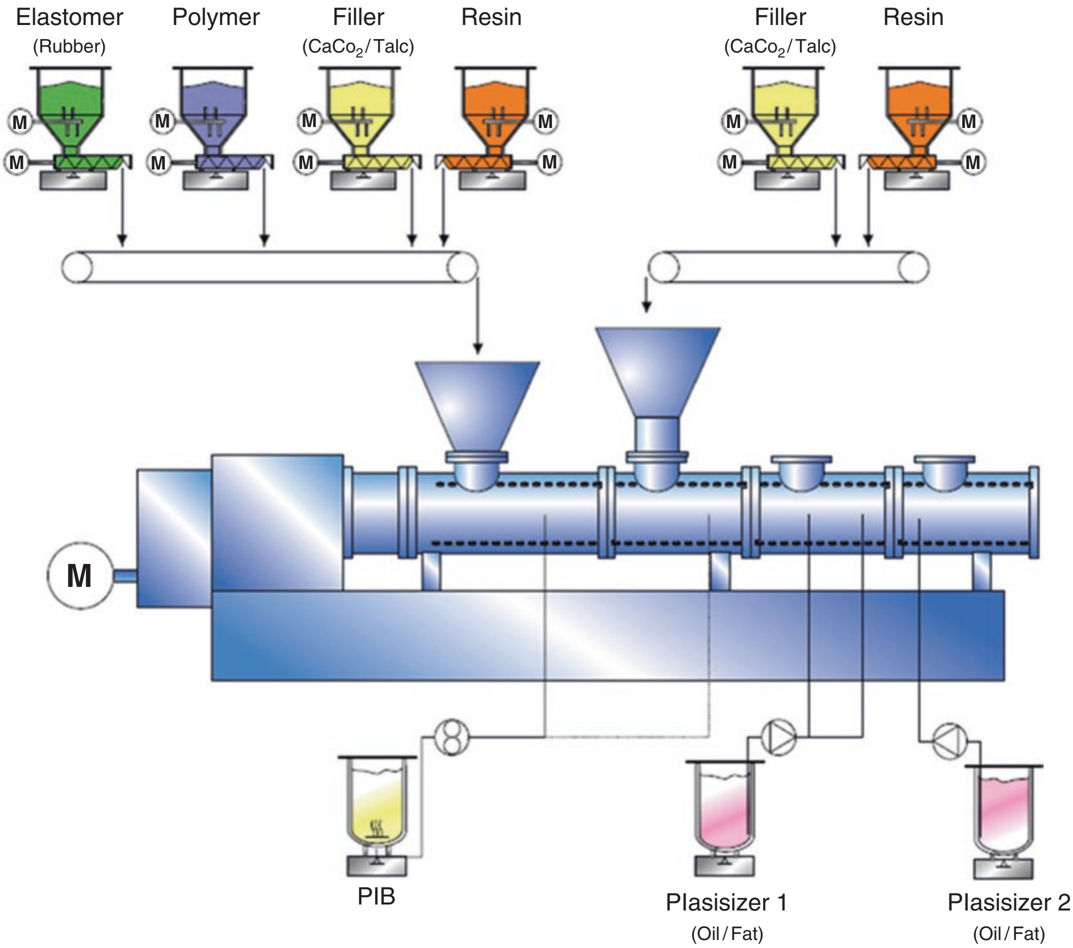

Figure 14.2 Continuous gum base manufacturing (Courtesy of Buss)

particles, given the same total amount of crystal powder added, give a firmer gum due to the higher surface area. If for some reason, the sugar particles have agglomerated, as might happen for example in humid environments, the sugar acts as if there were fewer larger particles and thus, the gum will be less firm than expected. These effects are not just important in consumer mouth feel, but are also important during processing (forming and wrapping) since the firmness at all temperatures will be affected similarly by particle size.

14.2.2.2 Dextrose

Dextrose powder is sometimes used to replace a portion of the powdered sucrose in gum since it is lower cost in some countries. Dextrose also has a greater cooling effect than sucrose when dissolved (see Section 2.3), providing benefit in certain types of gum. Dextrose is available in either anhydrous or monohydrate crystal powder forms. The difference in water content between the two forms is 8–10%, which can significantly affect gum properties. Glucose monohydrate powder is used in chewing gum since the anhydrous form pulls moisture out of the finished gum, making it too hard.

Because of the negative effects of glucose on gum properties, dextrose levels are usually less than 10%. All else being equal, the use of dextrose powder in gum typically results in a significantly firmer product than the equivalent amount of sucrose powder. Dextrose is also less sweet than sucrose (see Section 2.1).

14.2.2.3 Glucose Syrup

Glucose syrup in gum provides minimal sweetening; it is primarily added for its softening effect. It also acts to some extent as a humectant, depending on the DE used, since it contains water and some low molecular weight sugars. Glucose syrup is typically the only ingredient in sugar-based gum that contains water, so the amount of glucose syrup added and the water content (or Baumé) both influence the water activity of the final product and therefore, the ability to either pick up or lose moisture during storage.

In general, glucose syrup in the DE range from 38 to 44 is best for gum manufacture. In general, 38 DE glucose syrup is often considered ideal since it gives a gum product with minimal tack that is easy to process. Lower DE gives a firmer gum, whereas use of glucose syrup with higher DE leads to a softer, stickier product that is more difficult to process. However, whichever DE is chosen, it is critical that variations in DE from shipment to shipment are kept to a minimum so that gum properties are consistent.

As noted above, glucose syrup provides the water added in a sugar-based gum formulation. Thus, control of water content of the glucose syrup is critical to produce consistent product with the desired properties. Density (often expressed as degrees Baumé) is the parameter used to specify water content of glucose syrups (see Section 2.6). Higher density (higher degrees Baumé) correlates with lower water content. Glucose syrup is usually provided at either 43 or 45° Baumé (°Bé). Water content decreases as degrees Baumé increases, with 43 °Bé glucose syrup having approximately 19% moisture whereas 45 °Bé glucose syrup may be as low as 16% moisture. Glucose syrup with higher density (lower moisture content) is generally preferred in gum formulations since it gives a more desirable body and strength for chewing and processing. Again, it is important to minimize variations in density of glucose syrup from shipment to shipment to ensure consistent gum production.

One concern for use of glucose syrup in gum is that the residual sulfur dioxide (SO_2) level must be below 20 ppm (300–400 ppm is normal for glucose syrup used in other confections). Unlike most other candies, where SO_2 levels in glucose syrups are reduced by boiling, there is no such reduction step in gum processing. Thus, use of glucose syrup with a low SO_2 level ensures that the final gum product does not exceed the maximum of 10 ppm set by the World Health Organization (WHO).

14.2.2.4 Sugar Alcohols

Sugar-free gums are generally made with sugar alcohols, such as sorbitol, xylitol, mannitol, maltitol, and isomalt, among others. The physicochemical attributes of sugar alcohols are noted in Chapters 1 and 2. Those properties of particular importance for gum application include sweetness, caloric value, cooling effect, and cariogenicity (ability to inhibit tooth decay). Availability of the powdered form of a sugar alcohol and potential for recrystallization are additional factors of importance for consideration in sugar-free chewing gum.

Sugar alcohols provide some sweetness with about half (although this varies among polyols) the caloric value of sucrose (see Section 1.8.1). Because polyols are typically not as sweet as sucrose (see Section 2.1), they often require use of a high-intensity sweetener. Polyols have a laxative effect, meaning that daily consumption must be limited. Sugar alcohols also typically have a greater cooling effect than sucrose in the mouth as they dissolve (see Section 2.3), which can enhance the experience of chewing gum.

Sugar alcohols are noncariogenic, meaning they do not lead to tooth decay. Some polyols, like xylitol, may even act to prevent tooth decay by modulating mouth pH. This property has led to the many claims regarding sugar-free gum, particularly when made with xylitol. However, not all countries allow the same health claims.

As with sugar-based gum, the particulate nature of the polyol sweetener affects gum properties. Particle size must be in the proper range for adequate gum processability and so that initial mouth feel and texture of the gum are acceptable, yet do not cause the gum to be too firm. One of the most common sugar alcohols used in sugar-free gum is sorbitol. It is inexpensive and readily available in powders with different particle size. However, sorbitol can solidify into different polymorphic crystal forms, each of which can impart different properties to a gum formulation. In general, sorbitol is considered to make a firmer gum piece than other polyols, in part due to the size and shape of the crystalline particles, although one patent suggested that γ-sorbitol gave a softer gum and improved shelf life compared to other forms of sorbitol (DuRoss 1976). Sorbitol is also thought to undergo some sort of recrystallization in gum during storage, causing the gum to increase in hardness over time. Addition of mannitol and glycerin retard this recrystallization and extend shelf life.

Various other polyols may be used in sugar-free gum. Mannitol, because of its relatively higher cost than other polyols, is used at lower levels, if at all, in gum formulations. However, mannitol may be used to inhibit recrystallization of sorbitol or as a dusting agent because it is not very hygroscopic. It may also be used in the gum for its softening effects. Xylitol, despite its relatively high cost, is often used in sugar-free gums, especially where claims for its anti-cavity properties are allowed. To reduce costs, xylitol may be used in combination with other powdered polyols. With sweetness nearly equivalent to that of sucrose (see Table 2.1), xylitol-based gums do not require high intensity sweeteners. Isomalt and maltitol may also be used in sugar-free gum, but are more commonly found in the sugar shells of panned gum products.

Hydrogenated starch hydrolysate (HSH) is the sugar-free version of glucose syrup. When used in sugar-free gum, HSH serves the same functions as glucose syrup. HSH contributes water to the gum formulation and the aqueous sugar alcohols contribute functionality depending on their molecular weight. Smaller MW polyols, like sorbitol and maltitol, reduce water activity and act as humectants in gum, whereas the higher MW sugar alcohols contribute viscosity, reduce stickiness and retard post-production crystallization of polyols.

14.2.3 Acid

Fruit acids (citric, malic, fumaric, tartaric, etc.) are often added to gum to provide a tart or sour mouth feel and to enhance certain fruit flavors (see Section 6.3). Their use is necessary to provide high quality "true-to-fruit" flavored gums; however, acids can negatively impact gum quality and so their use must be carefully controlled. Special gum bases are designated for acid gums based on their resistance to the problems with acid addition. Calcium carbonate, a common texturizer, is a basic compound (pH above 7) that naturally reacts with acids. This acid-base reaction reduces the acidity of the piece and thus, the acid taste, or tartness, disappears. Also, the gum tends to be tackier and to fall apart when chewed. In tightly sealed gum packages or panned gum products, the carbon dioxide generated by the acid-base reaction can cause rupture of the package or coating. For these reasons, gums that will be used with acid flavors must be formulated with a nonreactive filler, namely food grade talc.

Acids are typically added at levels of 0.5–1% for flavor enhancement, although in products where a sour taste is desired, higher acid levels, perhaps up to 2%, would be used. Acids may impact shelf life through modification of water activity, and may affect color and flavor. Some colors are pH sensitive and addition of organic acids to gum can cause fading of colors; this is particularly a problem for certain "natural" red and blue colorings.

There are numerous organic acids to choose from. Citric and tartaric acids are often used in fruit-flavored gums to enhance initial flavor and provide a sour taste. These acids provide an intense tart sensation that quickly fades away. In order to extend the sour taste, malic or fumaric acids may be used since they have less immediate impact, but longer taste retention (see Section 6.3).

Sucrose in the presence of sufficient acid undergoes a hydrolysis, or inversion, reaction, where for each mole of sucrose present, one mole each of glucose and fructose are produced (see Section 1.3). This reaction is of most concern during heating, but reduced pH values can also promote inversion over time even at moderate temperatures. The generation of invert sugar in gum can potentially cause problems. Besides the stickiness that comes from invert sugar, a decrease in water activity will also result, which can cause sweating of the gum during storage or moisture pick up over time under high humidity conditions.

14.2.4 Humectants/Softeners

To soften the gum and extend its chewing characteristics, typically a humectant is used, with the most common being glycerin, liquid sorbitol or HSH. Glucose syrup also has humectant capabilities, particularly when higher DE syrups (with more low molecular weight sugars) are used. Humectants act to soften the gum by decreasing the viscosity of the gum base. Humectants also affect shelf life of gum through control of water activity. Addition of humectants reduces the water activity and slows the rate of moisture loss in drier climates. Humectants and softening additives may also affect flavor release by altering the partitioning ability of flavor molecules.

Levels of 0.3–0.5% glycerin are common in sugar-based gums, although up to 2% may be used for softer products. In sugar-free gums, the glycerin level is higher, from 3% to 7% (at times, up to 10–12%). Liquid sorbitol may be added at 0.5–1% in sugar-based gums, but may be as high as 8–12% in sugar-free gums.

Emulsifiers, such as lecithin, acetylated monoglycerides (ACETEM) and glycerol monostearate (GMS), may also be used in gum to provide certain advantages. Primarily, adding emulsifiers (1) tends to soften the gum, making it less tough and elastic, (2) provides lubrication during mixing, (3) reduces tack to teeth and (4) enhances flavor release. Due to the amphiphilic nature of emulsifiers (see Section 4.6), they soften gum by a different means than humectants. Gum base is generally hydrophobic, so a small amount of emulsifier can help promote mixing of aqueous-based ingredients (e.g., glucose syrup) and result in a softer product. Emulsifiers also enhance hydration of the gum (with saliva) during chewing, making the gum seem juicier. In bubble gum, emulsifiers (acetylated monoglycerides in particular) enhance the ability to form bubbles, producing a thinner bubble film, while also reducing the stickiness of the bubble.

14.2.5 Flavors

Flavors are added in gum primarily to provide the desired flavor experience. Without flavor addition, chewing gum would be bland. Flavor compounds enhance the eating experience through a combination of influences (see Section 6.2), with the main ones being taste and aroma. However, certain flavors may also influence the trigeminal nerve to stimulate effects such as warming/cooling and tingling.

Blends of compounds may be used to improve, complete or strengthen a desired flavor experience. Flavors might also be added to mask unwanted tastes, as might arise from the use of certain high-intensity sweeteners or addition of active components.

Many factors affect optimal choice of flavor in a gum system. Both type of gum base (acid or nonacid) and sweetener system are important considerations in choice of flavor. There is often a synergistic effect between flavor and sweetener that can affect flavor intensity, release, and recognition. The initial flavor release in chewing gum is correlated with dissolution of the bulk sweetener (Davidson et al. 1999). The relatively large amount of bulk sweetener used in gum means there is a uniform release of flavor as the sweetener dissolves. High-intensity sweeteners may also have an additional effect on flavor intensity and release. The quicker release of sweetness from high-intensity sweeteners (compared to the bulk sweetener) brings the flavor profile recognition more quickly to the palate. The blend of sweeteners helps create longer-lasting flavor recognition.

The interactions between gum base and flavor are very important since the gum base moderates flavor release. Flavors and their solvent carriers might also plasticize and soften the gum base, thereby affecting texture of the gum. If too much flavor is added to a formulation, the product may be unexpectedly soft and not process properly. It will also tend to fall apart in the mouth. On the other hand, too little flavor gives an unexpectedly firm gum that also may not process properly with poor flavor release. This is particularly true when propylene glycol is the only solvent in the flavor system. Other flavor solvents (i.e., oils, triacetin) and all active flavors have a better balance in the plasticizing effect of gum.

Both liquid and powdered forms of flavor can be used. If liquid flavors are used, oil soluble flavors are most common since they mix best with the gum base. However, the solvent that carries the flavor typically influences the rheological properties of the gum, generally acting as a softener, as noted above. Thus, highly concentrated flavors are best for gum application and powdered forms of flavors are common. Powdered flavors also tend to be more water soluble and therefore, are released more readily during chewing. For example, flavors may be encapsulated by spray drying the flavor molecule within a solid matrix (e.g., maltodextrins). As long as the spray-dried base material remains in the glassy state, the flavor is entrapped within. Over time, however, both the moisture in gum and certain types of flavor molecules (aldehydes, esters, alcohols, etc.) can degrade the encapsulant matrix, resulting in loss of flavor release characteristics. Once the base material dissolves, the flavor is released and solubilized in the gum base. Often, mixtures of liquid and powdered flavors are used to obtain the desired flavor release. Numerous methods of flavor encapsulation have been developed and an extensive patent literature exists on the subject.

Typical usage levels of flavors in gum are relatively high compared to other confections. Flavor levels may vary from 0.5% to 3%, although this depends to some extent on the type of flavor used. Liquid flavors are generally added at levels of 0.6–1.0%, whereas powdered flavors may be used at levels of 0.5–1.5%. Even at these levels, flavor duration in chewing gum may be as short as 4 min although flavor release over 12–13 min is typical nowadays with a combination of liquid and encapsulated flavors.

14.2.6 Colors

Generally, either liquid colors (soluble or dispersions) or color powders are used in gum. Soluble liquid colors should be dispersed in a solvent that mixes with gum base, like glycerin, rather than water or alcohol, so that they are uniformly mixed into the gum matrix. Water or alcohol based colors have limited solubility in gum base and are not used. One limitation of using glycerin, however, is that some dyes have very low solubility (<5%) so the concentration of dye that can be used is not very high.

Lakes, or liquid dispersions, (see Section 6.1) are often used in gum since they are generally quite stable and are retained in the gum base throughout the chew. The main concern is that they are completely mixed within the gum mass to give full and complete coloring of the product. Soluble dyes can bleed out of the gum base and color the tongue during chewing (which may sometimes be desired).

In gums with acid added, the stability of the color at low pH must be considered. Certain colors, particularly plant-derived "natural" flavors (exempt from certification), change hue depending on pH. The hue of anthocyanins, for example, changes from blue at basic pH to red at low pH. Other dyes may be degraded in acidic conditions, losing the desired coloring effect.

14.2.7 High-Intensity Sweeteners

Materials with sweetness significantly greater than sucrose are often used in gum to enhance sweetness levels without negative effect on texture and mouth feel. Some typical high-intensity sweeteners that may be used in gum include saccharin, aspartame, neotame, acesulfame-K (ace-K), cyclamates, and sucralose, although this list is not exhaustive (see Section 1.9 for more details on high-intensity sweeteners). High-intensity sweeteners are most often found in sugar-free gums since many polyols are not as sweet as sucrose, but they may also be used in sugar-based gums to enhance intensity and extend duration of sweetness. Levels of less than 0.5% are most common, although slightly higher levels may be used for example with aspartame since it degrades over time in the gum system.

The choice of high-intensity sweetener used in a particular gum formulation is made based on numerous factors. Stability in the gum system is one factor to be considered. Aspartame and neotame, as noted before, degrade over time in the gum and thus, shelf life is limited. Another factor affecting choice of sweetener is the rate of release in the mouth. Some sweeteners, like Ace-K, are quick to dissolve when consumed; they give an initial high intensity sweetness, which then fades very quickly unless it is protected through encapsulation. Synergistic effects on sweetness and flavor release may be observed when different high-intensity sweeteners are combined. High intensity sweeteners are often encapsulated in different carriers to release at different time intervals during chewing. In this way, both sweetness and flavor release of the gum may be extended for a longer duration chew.

With some high-intensity sweeteners, characteristic tastes are noted. These may be sometimes considered undesirable off-tastes or after-tastes. For example, a metallic bitterness occurs in gum if flavor has not been added; in this sense, flavor has another role, that of masking this bitter after taste while providing a recognizable flavor profile.

High-intensity sweeteners may also react with certain flavors. For example, aspartame reacts readily with the aldehydes commonly found in many fruit flavors (or cinnamon) and the degradation products no longer have sweetness. For this reason, at least in part, aspartame is often blended with Acesulfame K, which does not react with flavors so the profile can continue in the chew without the loss of flavor.

Various methods of encapsulating high-intensity sweeteners have been explored (and patented widely). These include spray-drying, extrusion processing, and even film coating. Encapsulation can help protect certain high-intensity sweeteners from degradation in the gum, but are primarily used to extend sweetness over time to enhance the chewing experience. Since flavor release goes hand in hand with sweetener release, extending the time over which the sweeteners release into the saliva provides a method of extending flavor life of a gum.

14.2.8 Active Ingredients

Gum has been used as a delivery vehicle for active ingredients for many years. Probably one of the most common active ingredients is nicotine – people trying to quit smoking can chew gum to reduce the desire. Gums that release digestive aids, like pepsin, have been commercialized for many years. Other active ingredients that have been incorporated into gum include dimenhydrinate (Dramamine), caffeine, and aspirin. There is even a patent for a chewing gum that contains Viagra®.

Numerous unique opportunities are available for delivery of active ingredients through chewing gum. For example, one approach to additives in gums is to decrease the likelihood of dental caries in a sugar-based gum. This might be done by either adding ingredients that neutralize the drop in pH or by influencing the microbial activity. Gums that release neutralizing agents, like carbamide or baking soda, can help prevent the drop in pH associated with chewing gum. Of course, sugar-free gums do not cause this pH decrease since the polyols are not metabolized by microorganisms. Xylitol, in particular, has been shown to be beneficial by increasing pH in the mouth. Gums that release anti-microbial agents, like zinc lactate, triclosan and chlorhexidine, can also be used to inhibit tooth decay, in this case by decreasing the microbial population responsible for tooth decay.

Gum is often used for teeth whitening, with a release of whitening agents during chewing. Baking soda, sodium stearate, polyphosphate, abrasives (zircon silicate), and enzymes (papain) can all be added for this purpose.

Numerous gums are available with nutraceutical properties. These include gums that deliver vitamins (i.e., Vitamins A, C and E), those that provide an ingredient for an energy boost (i.e., ginseng, caffeine, etc.), and those with important minerals (i.e., Ca, Mg and Zn).

Although these active compounds are present, depending on the molecular nature, there is some question whether they are fully released from the gum during chewing. Most notably, lipophilic compounds, such as the oil-soluble Vitamin E, may not be fully released from the gum base into the mouth since it preferentially remains in the more lipophilic gum base. As an alternative, these ingredients may be added in the shell of a panned gum piece. Further, through encapsulation, active ingredients may be protected to provide extended release over time. This is particularly important in, for example, nicotine gums, where the rate of release of the active compound is important to the beneficial activity of the gum. In one nicotine-containing gum brand, consumers are instructed to first bite the gum to begin release of nicotine and then to rest the gum against their cheek to allow adequate release time. This "park and chew" approach must be repeated to ensure proper release of the nicotine to deliver the desired dose. Various approaches have been developed (and patented) to provide proper release, through physical protection of the active to careful design of the gum base polymers to control partition coefficients and release rates.

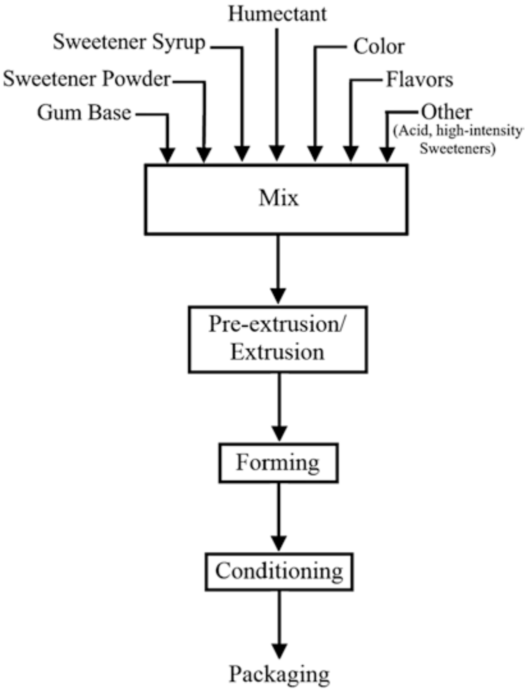

Figure 14.3 Schematic flow diagram of gum manufacturing process

14.3 Gum Manufacture

Gum production generally involves mixing all the ingredients together, forming the gum mass into the appropriate shape and then cutting to the desired size, as shown schematically in Figure 14.3. Gum production is usually a two-step process, where the gum base is made first, before the other ingredients are added to make gum. Once the gum base and other formulation ingredients have been mixed together, gum forming, cooling and packaging steps occur in a continuous, or semi-continuous, process. The process of mixing gum base with other ingredients may be either batch (e.g., sigma-blade mixer) or continuous (extruder). After mixing, the processing steps are slightly different for production of stick gums, ball-shaped pieces (filled or unfilled), chiclet pieces, and blocks (or chunks) of gum. Recent technological advances now allow a single-step process, where gum base ingredients and the other formulation ingredients are mixed together in a continuous mixing device. The gum mass is then formed, whichever process is used, and then the subsequent steps of cooling and packaging are the same.

14.3.1 Mixing

Gum mixing may be accomplished in either a batch or continuous process. Batch mixing is the traditional method, while continuous processing represents the future of gum manufacturing.

14.3.1.1 Batch Mixing

The first step in the traditional two-step gum manufacturing process is to mix gum base with the other ingredients into a homogeneous mass. A batch gum mixing machine is a high-torque unit with blades that scrape the inside surface of the mixing chamber. Often, the mixing device is a sigma-blade mixer that consists of two z-shaped blades rotating in opposite directions (Figure 14.4), although other designs may be used as well. Sigma-blade mixers are designed to uniformly mix high viscosity materials through careful design (length and shape) and operation

Figure 14.4 Typical batch gum mixer with sigma blades (with product head turned sideways in unload position) (Courtesy of Linden)

of the two blades. The two blades sweep closely past the walls to ensure minimal sticking. The capacity of batch gum mixers is typically 450–500 kg (≈1,000 lb) but may be as large as 1,000 kg (≈2,200 lb) per batch.

The gum ingredients are sequentially added to the mixer, starting with the gum base, to insure production of a uniform gum mass. Historically, gum base was melted and added to mixer in molten form. If the gum base is in block form, it is often pre-heated and softened prior to addition to the mixer. Alternatively, the gum base can be warmed directly in the sigma-blade mixer with steam jacket heating. Gum base in the form of sheets or pellets does not need softening and can be added directly to the mixer. After the gum base, other ingredients are added according to a prescribed protocol that involves sequential addition of (1) glucose syrup, colors and softeners, (2) half the powdered sweetener with glycerin (if added), and finally, (3) the remaining powdered sweetener with flavor. After each ingredient addition, the mass is mixed for a period of time (approximately 5 min) until the mass becomes uniform.

Temperature control in the mixer is necessary to ensure adequate uniformity of the ingredients although optimal temperature depends somewhat on the nature of the gum being produced. Typically, gum should be discharged from the mixer at about 45–55 °C (113–131 °F). Higher temperatures may be needed for firmer gum formulations; for example, gum balls may be mixed to temperatures as high as 70–75 °C (160–170 °F) in order to ensure proper consistency. If temperature of the gum in the mixer is too high, an excessive amount of powdered sweetener dissolves in the aqueous phase, which then causes problems when the temperature is reduced. For one, hardening of the gum occurs when the sweetener recrystallizes. Extended exposure to high temperatures can also cause degradation of the polymers, with negative consequences on gum characteristics. Since heating of the gum mass occurs due to mechanical heat during mixing, the mixing time must be controlled so that temperature of the gum does not increase too much. If dextrose monohydrate powder is added to the gum formulation, temperature should remain below 52 °C (126 °F) so that the water of hydration (monohydrate) is not lost. The water released from the dextrose crystals at these elevated temperatures causes the gum mass to get soft and sticky.

After mixing, the gum mass is generally cooled, or cured, prior to the forming step. This curing step allows crystallization of the particulate components as the temperature decreases to about 35–40 °C (95–104 °F). The gum becomes firmer due both to the cooling effect and the increased crystallinity. Storage conditions are typically 30–32 °C (86–90 °F) with low (45–50%) humidity.

14.3.1.2 Continuous Mixing

Gum mixing can be accomplished continuously through use of either a blade and pin mixer or a twin-screw extruder. In both cases, the raw materials are fed at appropriate points along the unit and, after shearing within the mixer, a homogenous gum mass exits, typically in the form of loaves for tempering prior to forming.

One of the most common continuous gum mixing systems is the blade and pin, or kneading, mixer. This is a single barrel unit with blades on the rotating shaft that slide between stationary pins attached to the outer barrel of the cylindrical mixer. The shear forces between blade and pin provide excellent mixing characteristics. By proper choice of geometry and orientation of blades and pins, the gum mixture is pumped to the end of the mixer barrel where it is collected for subsequent processing. Ingredients are sequentially added at points along the length of the kneader barrel. Temperature control along the barrel allows processing of temperature-sensitive products (e.g., sugar-free gum). Figure 14.5

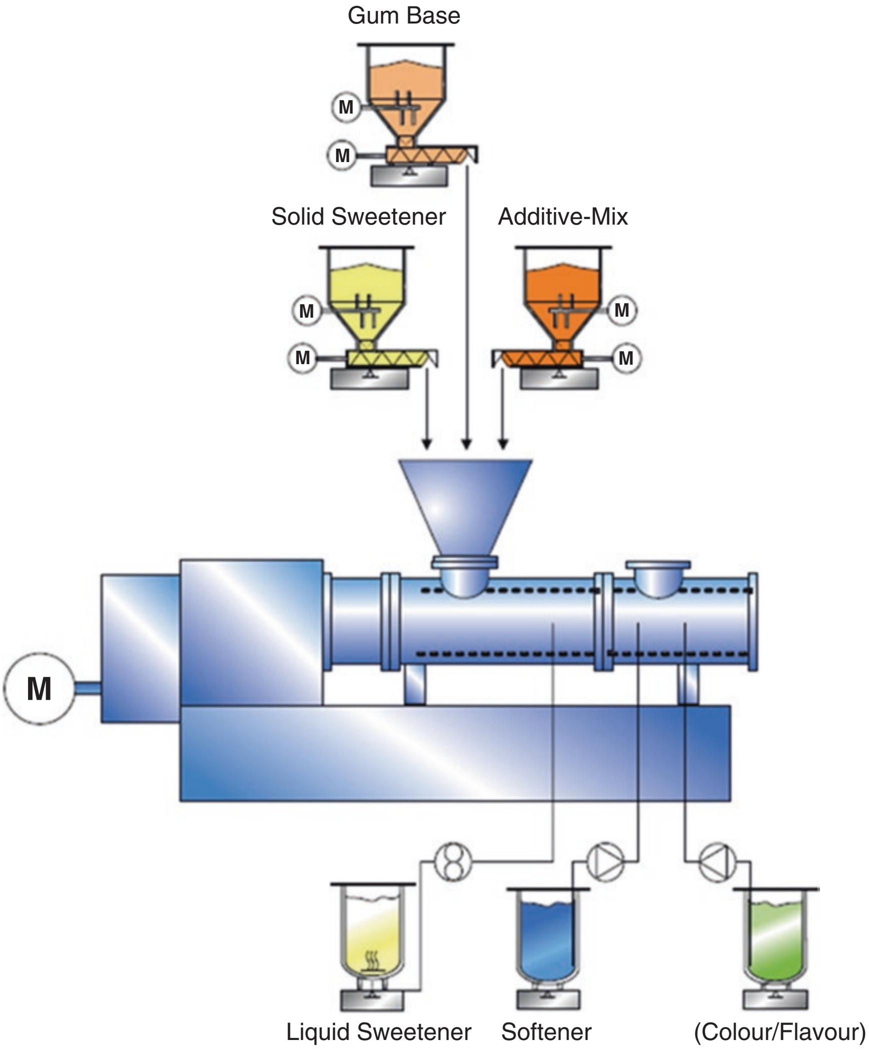

Figure 14.5 Kneader for mixing gum base (Courtesy of Buss)

shows how the various ingredients are fed into a kneading mixer to continuously produce gum.

Alternatively, a twin-screw extruder with co-rotating, intermeshing screws and kneading discs (called mixing heads) can be used for continuously mixing gum ingredients prior to forming. Gum base and powdered sweeteners are fed into the entrance of the extruder, with additional ingredients (liquid or solid) added under pressure at various stages along the length of the extruder. Gum base may be fed to the extruder in pellet form on a belt weighing conveyor or pumped in liquid form. Gum manufacturers that make their own gum base often use liquid gum base as feed to the mixing extruder. Accurate metering equipment (pumps for liquid ingredients and screws for powders) is needed to ensure that each ingredient is fed in at exactly the proper rate to produce the desired formulation. As with batch mixing, the order of ingredient addition is critical to forming a homogeneous gum mass. Sufficient mixing time within the extruder is needed between critical addition points.

A twin-screw extruder consists of two screw elements housed in a figure-eight shaped barrel, with each screw rotating in the same direction (co-rotating). The fully intermeshing screws are of the kind that continually wipe the surface clean so there is no sticking of gum material in the extruder. Temperature is varied along the length of the extruder to give the desired effect (softening, mixing, cooling, etc.) to the gum. In the early stages of the extruder, warm temperatures (about 50 °C/122 ºF) are needed to ensure that the gum mass is adequately mixed, with temperature reduced as it nears the exit, or die, of the extruder. Pressures of about 2,000–3,000 kPa (two to three atmospheres) are generated at the die for forming. A residence time in the extruder of several minutes is sufficient to add each of the ingredients and extrude a homogeneous mass of gum through the die for forming.

The advantage of continuous mixing comes from the efficient operation so that the entire process can be accomplished within minutes with large throughput rates (up to 7,000 kg/h) and reduced labor costs. Another advantage is that continuous mixing provides a guaranteed feed to a continuous sheeting or forming line. However, the capital cost of an extruder unit is significantly higher than batch mixing equipment. Typically, only high production gum manufacturing lines benefit from the advantages of continuous extrusion mixing.

14.3.1.3 One-Step Mixing

In both previous mixing technologies, gum manufacture was still a two-step process, where gum base was prepared separately prior to ingredient addition to form the gum mass. Since mixing of gum base is traditionally an energy intensive and time consuming process, it would be desirable to find ways to mix all the ingredients, both for the gum base and for the finished gum product, in one efficient mixing operation. To this end, newer technologies have been developed to allow mixing of all gum ingredients directly in one device to produce a homogeneous gum mass. That is, the components of the gum base (polymers, resins, fillers, etc.) can all be added directly into the mixer, along with the other gum ingredients (sugar powders, glucose syrup, flavors, etc.). Mixing may take place in either a batch mixer or continuous extruder, as noted above. The order in which the ingredients are mixed is important since it has been shown to affect finished product characteristics (hardness, tack, etc.).

The primary advantage of the one-step mixing process for gum manufacture is the reduction of energy costs in, first, producing the gum base and then, heating it back up again for mixing in the other gum ingredients during gum manufacture. One-step mixing can also simplify material handling logistics and reduce labor costs. Despite the benefits of one-step processing, however, the application of this technology is generally limited to gum manufacturers that produce large quantities of a few gum varieties.

14.3.2 Forming

Once the ingredients that make up the gum mass have been mixed and cured, the mass is formed into the desired shape by passing it through an extruder made of rotating screws that push the mass through a forming orifice, or die (sometimes called a nozzle). Each type of gum requires a slightly different process depending on the nature of the finished product. The forming extruder creates the general shape of the product (flat sheet, hollow tube, etc.) and then, after appropriate cooling or tempering, subsequent operations (sheeting, cutting, panning, etc.) provide specific characteristics and/or modifications to the finished product.

14.3.2.1 Stick and Tape Chewing Gum

Stick gum is one of the most traditional forms of gum and is relatively simple to make. After the gum ingredients have been mixed, the gum mass is extruded into a slab, rolled out into a thin sheet, cut into the desired shape, cooled, and then packaged. The process must be carefully controlled in order to ensure consistent product and to minimize problems.

After mixing, the fully cured gum mass is often first passed through a pre-extruder, which mixes and pulls the gum mass to develop a better stretch. The elastic properties of the elastomers in gum can cause problems with size control during extrusion forming and the pre-extruder helps minimize these shape problems. When pulled and stretched, the elastomers want to recoil. Pre-extrusion helps account for the size and shape changes associated with the recoil of the gum base elastomers. If a pre-extruder is not used, typically the gum mass must be cured prior to extrusion so that shape distortions do not occur during subsequent processing.

The pre-extruder is a screw device that forces the gum mass through the extruder die in the form of a thick sheet. The gum mass exits the pre-extruder at about 50 °C (122 °F) and is cooled to about 35–45 °C (95–113 °F), normally on a conveyor cooler. The cooled gum mass then goes into the forming extruder. In this device, a forming extruder (either a single screw or counter-rotating twin-screw) pushes the uniform gum mass through a slot die to form a thick sheet of gum, which is collected on conveyors that remove the sheet from the extruder at the same speed as it exits the extruder so there is no stretching.

The gum then goes through a set of rollers to reduce thickness (often called calendars or laminators). The gap between sequential rollers and the conveyor decreases to reduce the thickness, with each roller rotating at slightly different speed to maintain the gum sheet without stretching or folding. Precise adjustment of both the roller speed and the gap thickness is required to produce gum with a consistent thickness for packaging. Due to the elastic properties of the gum base polymers, if the gum is stretched during calendaring, it can “spring back”, somewhat like a rubber band, to become shorter and thicker than desired for gum sticks. Stretching the gum can also cause rips and tears in the sheet, particularly at the edges. The gum may also pass through a duster to apply dusting agent (i.e., powdered sweetener, talc, starch, etc.) to help prevent stickiness. After the sheet has been formed to the desired thickness, the gum passes through scoring rollers to provide break points for individual sticks after the gum has solidified. Control of the rolling and scoring section is critical since this is where thickness and length of the stick of gum is set. If each stick of gum does not have the exact length and thickness, problems will be encountered at the packaging station.

The scored sheets of gum are stacked on trays and placed in a conditioning room for several hours (or up to a day) to cool before cutting and wrapping. Temperature and relative humidity in the conditioning room are typically 17–20 °C (63–68 °F) and 40–50%, respectively. During conditioning, the gum becomes more firm as it cools and as crystallization of any dissolved sweetener is completed. If the gum is not sufficiently firm, problems will occur in the wrapping and packaging station.

After conditioning, the gum is sufficiently firm to be broken into sticks along the score marks. The breaking station also cuts the gum sticks into the correct widths and removes the trim at the edges of the sheet. Trim is reworked, usually by putting it back into the gum mixer, where it can help initiate crystallization of the gum mass. The gum sticks are now ready for packaging. The traditional package requires a relatively complex operation since each stick of gum goes through three separate packaging steps. First, a foil sheet is wrapped and folded around each stick. A paper sleeve is then placed around the foil wrap. Finally, multiple sticks are packaged into a well-sealed heavy paper and foil laminate package for protection from ambient conditions. More recently, stick gums are packaged in a paperboard box or envelope.

Any deviations in thickness, length or width of the stick of gum can cause problems with each of these packaging steps and thus, control of stick size is critical to smooth operation. Gum that is too firm or not firm enough will also not package well; thus, manufacturing conditions need to be controlled carefully to ensure a consistent texture at the point of packaging. Finally, it is critical to shelf life that each package be sealed properly to provide the necessary protection against moisture exchange with the environment.

Making gum in the form of rolled tape follows the same general process for making stick gum, except that the sheet is rolled onto a take-up reel before being cut. The sheet may be scored prior to rolling to allow easy break-up of individual rolls from the larger roll. Alternatively, individual rolls may be sliced from the larger roll with cutters similar to a bread slicer.

14.3.2.2 Hollow (or Filled) Gum Balls

To make gum balls, the homogeneous gum mass from the batch mixer is fed into a forming extruder from which a hollow tube of gum is extruded out of a cylindrical die containing a concentric plug in the middle of the orifice. The size of the internal plug sets the wall thickness of the final product so proper extruder operation is necessary to ensure that the wall thickness is controlled within tight specifications. The hollow rope of gum is often extruded vertically to allow the gum to cool and firm sufficiently to prevent deformation due to gravity. Low pressure air is pumped into the center to prevent collapse of the cylindrical rope. For filled gum balls, powders or jellies can be co-extruded into the rope through use of specially-designed feeders.

The warm rope of gum is then cut in a gum ball cutter (the same cutter used for creating the swirl on Starlight mints). A set of three rotating spindles cut the tube and roll the gum mass at the same time to form a hollow (or filled) ball. The plasticity of the gum as it is cut and formed is critical to forming a properly rounded ball with no cracks or deformities. Proper formulation and temperature control are important to ensure the gum mass has the desired plasticity as it is cut and formed. The gum balls fall onto a vibrating table, which keeps the gum balls rolling while they cool to set into shape. The gum balls are then conditioned (8–24 h) to allow them to completely solidify. The cooled and solidified gum balls are then sugar panned, as described in Chapter 13.

Packaging of gum balls depends on the method of distribution and sale. Often gum balls are sold in bulk, for example, to be filled in automatic dispensers (gum ball machines) or bulk bins. They may also be packaged in bags, boxes or single wraps.

14.3.2.3 Bubble Gum (Cut and Wrap)

Cut and wrap bubble gum starts out with a similar process as stick chewing gum. Again, the gum mass from the batch mixer is typically first fed to a pre-extruder to work the mass in order to avoid shape deformation in later steps. After cooling (to about 35 °C; 95 °F), the gum mass is fed into the forming extruder, which produces a steady rope of gum. Usually bubble gum comes out of the extruder as a rope in the desired shape, which is most often square or rectangular, but almost any shape can be produced by careful design of the die. Multi-color, co-extruded gum pieces can be constructed through the use of multiple forming extruder die heads.

When the gum exits the extruder, it has typically warmed up considerably due to the heat build up from viscous forces in the extruder. The rope of gum mass is conveyed through a cooling tunnel where it becomes firmer as it cools. The cooling tunnel also usually stretches the gum rope, sometimes by up to 75%, decreasing thickness or diameter. Proper temperature and humidity conditions are required in the cooling tunnel to ensure that the gum rope maintains a pliable texture without cracking or breaking. After cooling to about 25–35 °C (77–95 °F), dependent on the type of gum, the gum rope is ready for cutting and wrapping. An intact rope of gum is fed into the cut-and-wrap machine, where knives cut the gum into the desired pieces and wrapping arms apply the packaging material. A traditional form for cut and wrap bubble gum is the double-end fold package made, for example, from printed wax paper. When the gum rope is properly conditioned (size, shape and plasticity), up to 1,500 pieces per minute can be cut and wrapped. A dusting agent is often used to prevent sticking or gum build up on the machine.

14.3.2.4 Candy Coated Chewing Gum (Dragée, Pillow or Pellet)

Making dragée, or pellet, type gum pieces follows generally the same process as described for stick gum. The gum mass from the batch mixer is pre-extruded before being fed to the extruder where it is formed into a sheet. The same principles for pre-extrusion apply as noted previously. The continuous sheet is fed to a forming unit (calendar rollers) that rolls it into the desired thickness and cuts the sheet into the desired pieces. After passing through a cooling conveyor, the sheets are broken up in a tumbler. The pellets are allowed to cool in a conditioning room until they are sufficiently firm for tumbling in a pan coater. Application of a sugar (sucrose, dextrose) or polyol (maltitol, xylitol, etc.) shell and polish/glaze layer follow the general guidelines discussed in Chapter 13. After the coating layer has been formed and the polish/glaze layer allowed to set, the candy-coated dragées are sorted according to size to meet the desired specifications. Candy-coated gums may be sold in bulk, filled into boxes for sale or packaged in blister packs.

14.3.2.5 Gum Filled Hard Candy

Some gum pieces are coated in hard candy to provide a unique textural characteristic, with a brittle hard candy exterior and chewing or bubble gum inside. Such pieces are often sold as lollipops with the gum-filled hard candy posted on a stick. Gum-filled hard candy can be made either with the manual rolling method or by pumping the gum mass into the hard candy cylinder prior to roping. Careful control of temperature, moisture content and water activity of both gum and hard candy are required to minimize potential problems during formation and storage.

In the traditional manual process, similar to the process used to make cut rock (see Chapter 8), a cylinder of gum mass is covered with a layer of plastic hard candy mass. The gum-filled hard candy cylinder is then placed onto the batch roller (see Section 8.3) for forming. Alternatively, the gum mass can be pumped directly into the plastic hard candy cylinder through a lance in the batch roller or both gum and hard candy can be pumped through a die to form the rope. In either method, a rope with hard candy on the outside and gum within is formed on the batch roller. The rope is fed through a series of rope sizers before entering a cutting device where the pieces are formed and a stick is added to make a lollipop. The pieces proceed through a cooling tunnel to solidify both hard candy and gum. After solidification, the pieces are individually wrapped.

Control of temperature and moisture are necessary to prevent problems in hard candy-coated gum products. First, the gum must be warm (60–65 °C; 140–149 °F) to avoid thermal shock when it first comes into contact with the hard candy mass. If the gum is too cold, the hard candy in contact with the gum will quickly cool to the point where it is no longer pliable; it is then likely to crack. Second, to avoid moisture migration during storage and the resulting problems of graining, the water activity of the gum must be as close as possible to that of the hard candy. Since the water activity of gum is usually about 0.5–0.6, whereas hard candy has a water activity of about 0.3, the gum must be formulated to lower water activity to an acceptable level without making it too firm.

14.3.2.6 Other Types of Gum

A wide variety of novel gums have been produced over the years. These include shredded gum, paste gum, gum suitable for depositing, and even powdered gum for compressed tablets. Each of these gum types places unique requirements on the gum base and/or the finished product. Shredded gum, for example, must be adequately protected from sticking together, usually with a dusting of nonstick powder (i.e., sugar or sweetener, talc or starch). Paste gum contains high levels of syrups and solubles that quickly dissolve in the mouth to allow the gum bolus to form. Gum powder for compressed tablets can be made by either cooling a traditionally-made gum in a high shear mixer or by grinding specially-formulated gum into a powder. The powder is then compressed into a tablet (see Chapter 7).

14.4 Product Characteristics

The properties of chewing and bubble gum arise from the specific combination of ingredients. Synthetic (or natural) food-grade rubbers with various modifiers plus the dispersed crystalline sweetener phase affect properties such as chewing characteristics, bubble-blowing capability and flavor release.

14.4.1 Gum Microstructure and Physical Properties

Gum is an extremely complex material, made primarily of powdered sweetener and gum base with numerous other ingredients distributed throughout the gum mass. The physical properties of gum are dependent on the amount and nature of each of these ingredients and the structures they form, as governed by the processing conditions.

In any discussion of gum properties, it is necessary to distinguish three different stages: (1) gum base itself, (2) commercial gum after addition of all ingredients, and (3) the gum bolus during and after chewing. At each point, additional ingredients are added (or removed) that change the characteristics of the product at that point.

14.4.1.1 Gum Base

The continuous structure of gum is primarily made up of gum base, a complex mixture of ingredients (see Table 14.3). To a large extent, the properties of chewing and bubble gum are due to the nature of the gum base. The composition of gum base was covered in detail in Section 14.2.1. Here, the structural elements of gum base will be discussed. Polymer science principles are important to understanding the properties of gum base; however, very little has been written about the specific aspects important to gum properties.

Polymers of butadiene, styrene and isobutylene make up the synthetic rubbers used most frequently in gum base. The extent of polymerization, or co-polymerization, plays a significant role in determining the characteristics of the final product. The types of rubbers used (chemical structure, molecular weight, degree of branching, etc.) and the nature of the other base ingredients determine the physical characteristics of gum.

Perhaps one of the most important characteristics for chewing and bubble gum is its viscoelastic nature. Elasticity occurs when the amorphous coils of the rubber molecules stretch and then spring back upon release of the stress. Many synthetic rubbers are designed (through cross-linking) to be highly elastic. These rubbers give the recoil properties of, for example, rubber bands. In gum base, such a high degree of elasticity is not desired and thus, the rubbers used in gum base are not cross-linked. This gives a viscoelastic material with a balance of viscous, or plastic, properties and elastic characteristics. The choice and amount of rubber polymers used in the gum base, along with the choice of texture modifiers, are varied to govern the specific elastic characteristics of a gum product. For example, to make a softer gum, one approach would be to decrease the amount of butyl rubber (a high molecular weight component) in the base and/or increase the content of polyisobutylene (PIB) (with lower molecular weight). Additional plasticizers could also be considered to soften the gum base.

The choice of polymers also determines bubble blowing ability of a gum. In bubble gum, tear properties under tensile stress are important. Typically, bubble gum contains higher levels of high molecular weight polymers, such as styrene butadiene rubber (SBR) and butyl rubber (IIR), and increased levels of plasticizers. These ingredients increase elasticity and allow a bubble to be formed and held. According to Lee (2001), a good bubble blowing gum base should have a tan (δ) value greater than 0.6 (measured at 45 °C and 10 rad/s). Since tan (δ) is the ratio of loss modulus (viscous characteristics) to storage modulus (elastic properties), a bubble gum base should have slightly greater elastic nature than viscous nature. Lee (2001) states that a gum base with too much elastic nature, with tan (δ) less than 0.6, does not provide good bubble-blowing characteristics.

As noted earlier, gum base is a complex multi-phase material from a structural standpoint (Lee 2001). There is a heterogeneous amorphous matrix comprised of a continuous nonpolar elastomer network with discrete regions of polar elastomer dispersed throughout. Gum base also contains finely ground mineral particles dispersed throughout the amorphous matrix in addition to semicrystalline regions of lipid and wax. A photomicrograph of gum base can be seen in Figure 14.6. Discrete globules of PVAc can be seen distributed throughout the continuous polymer matrix, along with a large number of fine filler particles. Again, this combination of amorphous continuous phase and various particulate fillers determines the chewing characteristics of the gum.

As noted earlier, the amorphous polymer phase also contains a distributed crystalline phase of hardened fats or waxes. Differential scanning calorimetry (DSC) has been used to document this crystalline behavior of gum base (Lee 2001). As seen in Figure 14.7, there is an endothermic peak at about 52.5 °C (126.5 °F) indicative of melting of the hardened fats and/or waxes present. This crystalline network is necessary to prevent cold flow of the gum base. The elastomers themselves do not have sufficient solid-like characteristics to stand up to the weight of gravity and will undergo cold flow.

One important physical property of gum is the softening point. Loosely defined, the softening point is the temperature at which the gum base transitions from primarily a solid-like to a more liquid-like state. In general, softening point is decreased with rubbers that are lower molecular weight and with higher addition of softening agents (lower T_g) . The rubber components in gum, butyl rubber (IIR) and polybutadiene (SBR), have very low glass transition temperatures, on the order of −35 to −40 °C and −50 to −60 °C, respectively. It is the addition of components like polyvinylacetate (PVA) and rosin esters that increase T_g of gum base. Figure 14.8 depicts the approximate change in elastic modulus (G′) of a dry gum base when heated (Lee 2001). At 25 °C (77 ºF), the gum base has solid-like characteristics (high G′ value) with a rapid softening in the temperature range between about 35 and 45 °C (95–113 °F). It is molten above temperatures of about 50 °C (122 °F). When plasticized with flavor, as in a finished chewing gum, the melting temperature range will be slightly lower so that the gum softens at mouth temperatures during mastication.

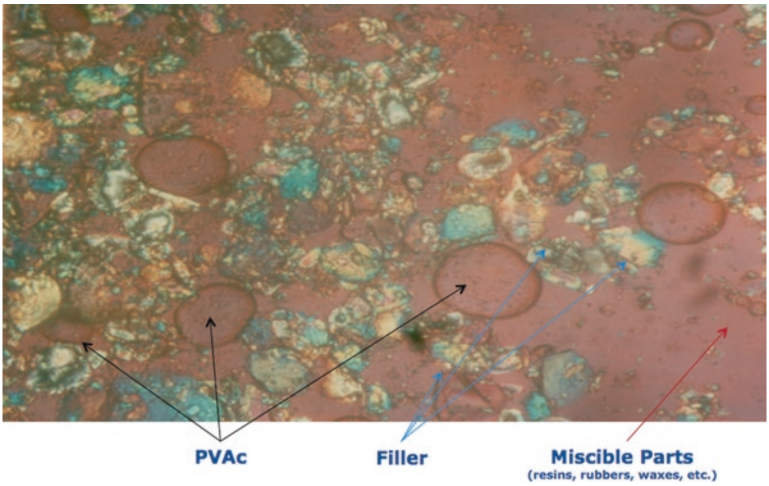

Figure 14.6 Photomicroscope image of gum base showing different microstructural elements

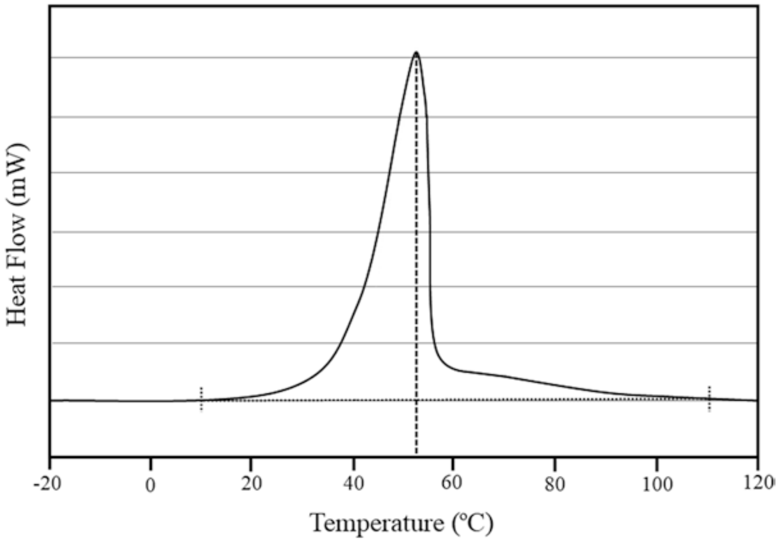

Figure 14.7 Differential scanning calorimeter *curve* of gum base showing melting exothermic transition of crystalline lipids and waxes (Adapted from Lee (2001))

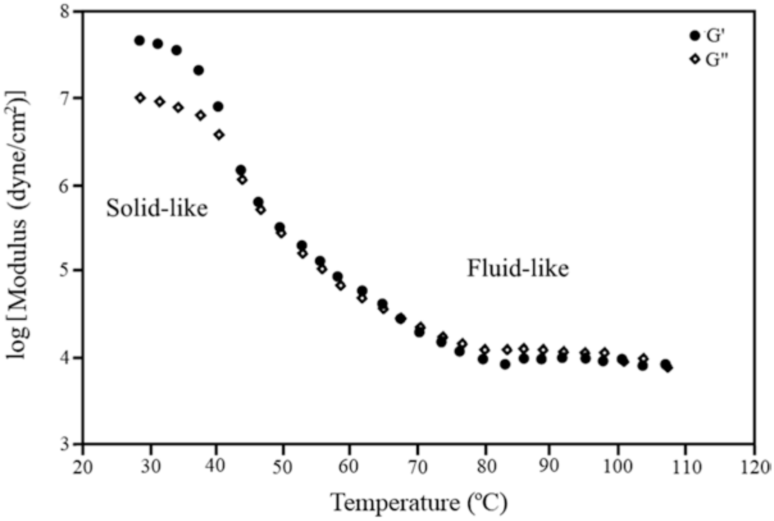

Figure 14.8 Elastic modulus of gum base with increasing temperature showing softening temperatures (Adapted from Lee (2001))

14.4.1.2 Gum Before Consumption

In addition to the heterogeneous structures found in gum base (previous section), a finished gum product also contains dispersed particulate sweetener and other ingredients. In commercial gum, the most abundant ingredient, the particulate sweetener, makes up between 50% and 60% of the gum mass (compared to only 15–25% for gum base). Thus, commercial gum is a high phase volume particulate product with the particles held in place by the complex gum base structure.

The crystalline bulk sweetener is there mostly to provide sweetness, but it also affects physical properties (firmness, etc.) of the gum product. When the powdered sweetener and liquid elements (glucose syrup or HSH) are mixed with gum base to form gum, some of the powdered sweetener dissolves in what little water is present. Despite this small amount of dissolution, the majority of the powdered sweetener remains as dispersed crystalline phase.

For the best consumer perception, gum should undergo a transition from more solid-like to more fluid-like after being put into the mouth. Body heat should be sufficient to soften gum considerably to make it easier to chew (although hydration by saliva also helps soften the gum). At room temperature, gum should be firm but pliable, whereas at body temperature, gum should soften considerably to allow good chewing characteristics. This softening is due in part to the melting of the crystalline fat in the gum based and the solid-like to fluid-like transition. This transition occurs over a broad range of temperatures, with the transition often starting at about 10–12 °C (50–54 °F) and finishing at about body temperature, 37 °C (98.6 °F).

Various gum ingredients interact with the gum base and can also change its properties. One in particular, oil-based flavors, probably one of the main reasons people chew gum, can have a significant effect on gum properties by plasticizing the gum base, reducing its glass transition temperature, and softening the finished product. Formulations, including gum base characteristics and flavor amount/type, need to be carefully constructed to give products with the desired chewing characteristics.

The unique rheological properties of chewing and bubble gum have been documented recently by Martinetti et al. (2014). A thermal scan of several commercial chewing and bubble gums showed a softening point at around 37 °C (98.6 °F) with a significant decrease in modulus between 30 and 40 °C (86–104 °F). Bubble gums had a significantly lower elastic modulus (two orders of magnitude) than chewing gums, indicative of the types of elastomers used in the gum base. At all conditions, the gums were more solid-like than fluid-like ($\tan\delta < 1$), although there was variability among samples. The chewing gum example had significantly higher G' up to about 30 °C (86 °F) during heating, after which G' and G'' were closer in value (increased fluid-like behavior) even though G' remained higher than G''. The bubble gum example had G' slightly larger than G'' throughout the temperature sweep. Based on an amplitude sweep, the linear viscoelastic region was quite low, less than 1% strain. Upon greater deformation, the gum was not able to return to its original structure, a phenomenon attributed to the nature of the small filler particles in gum. In a frequency sweep, the gums exhibited a stiff gel-like behavior, at least at small deformations. The gums also exhibited strain-hardening upon uniaxial extension, most likely caused by the particulate nature of the sweeteners. As expected, bubble gum withstood larger stresses than chewing gum before rupturing upon being pulled apart.

14.4.1.3 Gum Upon Mastication

Once the consumer puts the gum piece into the mouth and begins to chew, gum properties change dramatically. The powdered sweetener dissolves quickly (within 1–3 min) in the saliva and releases a significant amount of flavor. At the same time, saliva hydrates the gum and changes the chewing properties of the bolus. The water content of the bolus increases by perhaps 5–10% during hydration in the mouth, which reduces glass transition temperature. However, solubilization of plasticizers out of the gum bolus and into the saliva during hydration may produce the opposite effect, tending to increase the glass transition somewhat. The net effect, particularly due to the dissolution of powdered sweetener, is a significant softening of the gum during hydration in the mouth.

For consumers, the chewing characteristic of the gum bolus is of primary concern; however, the myriad parameters that affect the consumer's chewing experience make detailed discussion of specific relationships quite difficult. Parameters of importance to the consumer during chewing of gum include hard/soft texture and chew, bounciness/elasticity of the bolus, the consistency of the chew (does not significantly harden or soften during the chew), and the cohesiveness of the bolus during chewing. Further, the importance of these textural properties on flavor release is of considerable importance to gum manufacturers.

14.4.2 Flavor Release

In general, flavor release from a confection into the mouth is governed by two factors: (1) the thermodynamic partitioning of flavor molecules between the food matrix and air and saliva in the mouth and (2) the kinetic rate that the flavor molecules migrate between the different phases, or the mass transfer rate (de Roos and Wolswinkel 1994; Ovejero-Lopez et al. 2004). In the initial period of chewing (about 1–3 min), flavor release is influenced heavily by the dissolution of sweetener into saliva, whereas in later periods of chewing (greater than 10 min), once the sweetener has been completely dissolved, flavor molecules must be extracted by either saliva or air in contact with the gum (de Roos 2003).

The partitioning of flavors between gum base, saliva and air is particularly important in gum because of the strong interactions between flavor molecules and gum base. Due to this partitioning of flavors in gum, saliva and air, a considerable portion of the flavor, over 50% of the initial amount added, depending on the hydrophobic characteristics of the flavor, remains in the gum base even after extensive chewing. It is for this reason that flavor levels in gum are higher than normally used in other confections.

Many flavors used in gum are preferentially more soluble in the hydrophobic gum base than they are in water, so they tend to remain in the gum base rather than being released during chewing. The preference of a flavor molecule to remain in the hydrophobic environment of the gum base or the hydrophilic environment of saliva is expressed according to a partition coefficient. The partition coefficient of a flavor is found by equilibrating a lipid phase in contact with an aqueous phase. The ratio of the flavor molecule concentration in each phase gives the partition coefficient. Hydrophilic flavor molecules have higher concentrations in the aqueous phase (higher partition coefficients for water to gum) and hydrophobic flavor molecules are found preferentially in the lipid phase (lower partition coefficients for water to gum).

de Roos (2003) studied the release of several flavor molecules with a range of partition coefficients during chewing of gum. In the first 10 min of chewing, when flavor release was enhanced by dissolution of the sweetener (a hydrophilic material), the extent of release of flavors was dependent directly on the partition coefficient. That is, the more hydrophilic flavors were released to a greater extent and the more hydrophobic flavors showed significantly less release, with less than 10% flavor release for the most hydrophobic flavor studied (ethyl cinnamate). During the second 10 min of chewing, where flavor must be extracted from the gum base (dissolution of sweeteners has been completed) by the saliva, release rates were not entirely dependent on partition coefficient. That is, there was no direct correlation between release and partition coefficient. The complex behavior of flavor release in this study was related to the complex interactions between gum base, saliva and air during chewing.

As noted above, the diffusivity of a flavor molecule through the gum as it is hydrated during chewing also plays a major role in flavor release. As the gum is chewed, the flavor diffuses from the cud into the saliva or into the air, where it is detected in the nose by the olfactory system. Diffusivity is a function of molecular weight, with small molecules typically diffusing most rapidly. However, diffusion is also influenced by the molecular interactions with the matrix and these interactions may govern how fast a flavor molecule diffuses through the gum. The process of chewing also enhances migration of flavor from the gum to the mouth as the piece is chewed since new surfaces are exposed from which flavor can diffuse.

The microstructure of the gum also influences diffusion and thereby, affects flavor retention and release (de Roos 2003). Various microstructural attributes of gum, including for example the amorphous/semi-crystalline structure of the gum base, hardness, sweetener particle size, and water content can significantly affect flavor release. For example, sensory perception of perceived flavor intensity of menthone during gum chewing was found to correlate better with sucrose dissolution and release than the actual volatilization of menthone during chewing (Davidson et al. 1999). That is, perceived flavor intensity decreased at the same rate as sweetness decreased due to sucrose dissolution even though measured menthone concentration in the breath remained high even after the sweetness had been exhausted.

Poteneni and Peterson (2008a) found a similar correlation between flavor release and dissolution of sorbitol in a sugar-free chewing gum. Poteneni and Peterson (2008b) went on to show that the release of cinnemaldehyde from gum followed a two-step process, with the first step being governed by dissolution of the sweetener (sorbitol) and the second step being governed by the partition coefficient of the flavor molecule.

Hardness of gum affects flavor release (de Roos 2003), with softer gum giving greater flavor release. The increase in diffusion rate in the softer matrix is most likely responsible for this effect. Gum with an emulsifier (5% glycerine monostearate) added to act as plasticizer also led to greater flavor release. Even the efficiency of chewing by the consumer has been shown to influence flavor release (de Roos 2003), with more vigorous chewing leading to enhanced flavor release. Clearly, there are numerous factors that influence flavor release in gum.

Enhancing initial flavor release and extending flavor release over a longer time have long been the goals of the gum industry. In general, gum loses the majority of its flavor intensity within the first few minutes (which tracks with dissolution of the sweetener), so gum makers seek to extend that time for as long as possible while still providing a profound initial flavor experience. Numerous methods for these goals have been explored over the years, with various flavor and/or high-intensity sweetener encapsulation methods being the primary approaches investigated. Encapsulation of flavors in a hydrophilic matrix typically allows faster and more complete flavor release than when the flavors are simply added into the gum mixture. de Roos (2003) found that spray-dried flavors encapsulated in a hydrophilic matrix had significantly faster and more complete flavor release than when the flavors were simply mixed into the gum. Prior to chewing, the spray-dried matrix inhibited the flavor molecule from associating with the gum base, but to an extent depending on the flavor's partition coefficient. The more hydrophobic flavor molecules were seen to diffuse more readily from the spray-dried particle into the gum base, which ultimately reduced their flavor release compared to the more hydrophilic flavor molecules. Upon chewing, the encapsulating material dissolved into the saliva, allowing immediate and more complete release of the flavor.

To extend flavor release during mastication, encapsulated high-intensity sweeteners are often used. Flavor release is enhanced by the release of sweeteners, so if release of sweeteners can be delayed, so can the release of flavors. Encapsulation of flavors in nonhydrophilic carriers can also delay flavor release. Many of these technologies are either patented or proprietary.

Continued research and development to better understand the mechanisms of flavor release and perception during gum chewing is likely to yield gums with substantially extended flavor release.

14.4.3 Shelf Life

Probably the most critical shelf life issue in gum is moisture gain or loss during storage. Despite the low water content, the water activity of gum is typically about 0.5–0.6, so storage at lower relative humidity (RH) results in gradual moisture loss. As moisture is lost to the air, the gum gradually hardens in storage. Storage at high RH results in moisture uptake, which causes the gum to become soft and sticky. The speed of moisture change depends primarily on the external conditions (temperature and RH) and the nature of the packaging material to act as a moisture barrier. Extremely dry (RH<30%) or humid (RH>70%) conditions lead to rapid moisture change unless packaging materials with excellent water barrier properties are used.

Moisture loss leads to harder gum for two reasons: (1) the gum matrix itself becomes harder due to the drop in moisture and (2) recrystallization of the sweetener results in added crystal dispersion, even leading to bridging between crystals. In sugar-free gum made with sorbitol, for example, recrystallization occurs during storage when moisture content changes. If the gum loses moisture, sorbitol crystallizes out of the liquid phase to maintain phase equilibrium. The combination of moisture loss and additional sorbitol crystallization causes the gum to harden over time. Typically, addition of mixed polyols minimizes problems of recrystallization. For example, addition of mannitol helps prevent sorbitol recrystallization during moisture changes, extending shelf life. Similar effects are seen in sugar-based gum.

Shelf life testing for gum is often done under the conditions that will be found during normal storage. In some cases, low RH (30%) is important, whereas in other cases storage is under humid conditions (75%). Because of the extended length of time to end of shelf life under most normal storage conditions, accelerated tests are most usually done, where conditions are pushed to extremes to force moisture migration to occur at a faster rate. However, accelerated storage studies must be done with caution; specifically, in order to gain useful knowledge about shelf life, the mode of failure must remain the same under accelerated conditions. Sometimes, pushing temperature and RH to extreme conditions causes a different mode of failure so that results from accelerated tests do not match those seen under normal storage conditions.

During shelf life testing, several physical attributes of the gum are measured. Besides the visual and organoleptic aspects of the gum, weight changes and physical properties are measured. Weight loss or gain is dependent on the difference between the water activity of the gum and the storage humidity. The greater this difference, in general, the more water will be lost or gained and the faster it will occur. Physical properties of the gum are also measured during storage. Flexibility of a stick of gum can be quantified by applying sequential compression and tension forces, and counting the number of cycles needed for the gum to crack. Softer gum takes more cycles before it cracks. Hardness of gum can be measured by a penetrometer, measuring the force required to penetrate the gum to a specific depth under specific conditions. The maximum force of penetration correlates with the hardness of the gum piece. Further refinement of this method can give the different levels of hardness during initial (1–10 s of consumption), intermediate (10–60 s) and final (1–5 min) chewing characteristics. Penetrometer can also be used to measure stickiness or the tack to teeth. In this measurement, the probe is an artificial tooth made of polymeric material that penetrates into the gum and is then removed, all at standardized conditions of speed and penetration depth. The forces measured during compression and removal of the tooth from the gum correlate to hardness and stickiness, respectively.

In panned gums, moisture migration between gum and sugar shell can also lead to negative changes that reduce shelf life, particularly when external conditions are abusive (high temperature and excessively high or low RH). The water activity of a sugar shell (perhaps 0.3–0.4) is typically less than that of the gum inside (about 0.55) and this difference in water activity leads to moisture migration over time from the gum to the shell. Moisture migration continues until the two zones, shell and gum, attain equilibrium when they both have the same water activity. The consequences of this migration are hardening of the gum and softening of the shell (loss of crunchiness). Temperature, RH of the storage environment, and the water barrier properties of the package material also affect the rates of moisture migration and affect the shelf life of panned gum products.

14.5 Troubleshooting

Problems associated with chewing and bubble gum generally relate either to texture or flavor, although other problems include shape retention (e.g., gum balls), piece size/density, and cud size. Textural problems include such characteristics as firmness/hardness, stickiness, and grittiness as well as bubble blowing characteristics in bubble gum.

14.5.1 Imperfect Shape

The shape of the gum piece is an important quality parameter, which may be influenced by processing conditions. For example, gum balls may not be perfectly round if not cooled properly. If gum is not sufficiently mixed and allowed to relax, the elastic nature of the gum base polymers may cause the piece shape to be deformed.

14.5.2 Gritty Texture

Gum should be homogeneously mixed, without lumps, and provide a smooth chewing characteristic. Proper mixing of gum ingredients is necessary to ensure homogeneity, although over-mixing can lead to other textural problems. Gum base and any reworked gum product should not be too old as this can cause problems of inhomogeneity and lumpiness. Grittiness of gum is also related to sweetener particle size; proper powder size is needed to ensure smooth chewing characteristics without negatively affecting other textural properties.

14.5.3 Gum Too Hard or Too Soft

Gum that is too hard or too soft can have numerous ingredient causes. Gum base, glycerin, corn syrup (or maltitol syrup), water, flavor, emulsifier or sweetener powder content, and sweetener particle size are among the many parameters that influence gum texture. To reduce hardness of gum, more water, glycerin, flavor or corn (or maltitol) syrup can be added, lower Baumé syrup can be used, or less sweetener powder can be added. The reverse trends lead to harder gum. Operating procedures that can influence texture (too hard or soft) include overmixing and overheating of the batch. Proper gum conditioning is also necessary.

14.5.4 Cud Too Small or Large

Characteristics of the gum piece and the bolus during chewing are related primarily to the relative contents of gum base and other ingredients. Sufficient gum base per piece size is required to ensure that the size of the cud is appropriate. Smaller pieces require a higher percentage of gum base (25–30%) to ensure a minimum cud size. Reducing gum base content is required if the bolus is too large.

14.5.5 Poor Bubble Blowing Capability

Bubble blowing characteristics of bubble gum are primarily related to the nature of the polymers in the gum base, although processing can also have negative effects on bubbles. If bubbles are too small, the gum base content should be increased. If gum base content is appropriate yet bubbles are too small, over-aged gum base or over-heating of the gum may be the cause. High levels of oil-based flavors may also cause small bubble size. Addition of an emulsifier and avoiding use of water-based flavors may help increase bubble size.

If the bubble sticks to the lips or teeth, the gum is generally too soft. Increasing gum base level can help as can reducing flavor level and addition of emulsifier.

14.5.6 Poor Flavor Release/Retention

Proper flavor release is one of the most important aspects of chewing and bubble gum. Gum should provide a quick burst of flavor that does not disappear too rapidly during chewing. As noted in Section 14.4.2, many factors influence flavor release in gum, from the nature of the flavor (through its partition coefficient) to the nature of the gum matrix itself.

Processing parameters may influence flavor retention and release. If gum is overheated during manufacture, flavor intensity and profile will potentially change as volatile flavors are lost and/or flavor molecules react. Gum mixing must be adequate to completely and uniformly mix the flavor into the gum mass.

The flavor carrier solvent (propylene glycol, etc.) must be chosen carefully to ensure proper flavor release without negative effects (softening) on gum texture. Flavor levels must also be chosen to provide adequate release during chewing since a high percentage of the more hydrophobic flavor molecules are retained in the bolus during mastication. The use of encapsulated flavors and sweeteners can enhance and control flavor release.

14.5.7 Loses Color/Fades

As noted in Section 14.2.6, some exempt from certification (“natural”) colors can change in hue due to environmental conditions, notably pH. Making sure the pH is correct for the type of flavor used will help prevent color changes. Use of lake colors also helps promote color stability.

14.5.8 Sweating Gum

If mixing is sufficient to completely incorporate aqueous ingredients, gum sweating is most likely due to moisture sorption from the air. This could occur either because the storage conditions are too extreme for the moisture barrier properties of the package or because the water activity of the gum is too low. Given that the package is acting correctly to protect against warm, humid conditions, techniques for raising water activity include reducing humectants (e.g., glycerin), adding less aqueous sweetener or higher Baumé or lower DE glucose syrup, and raising the bulk sweetener. Dusting powder and/or emulsifier (lecithin, glycerol monostearate) may be added as well to prevent sweating.

14.5.9 Sticky Gum

Stickiness in gum can arise from the same reasons that lead to soft or sticky gum (as listed above). Stickiness can cause problems both in manufacturing (gum sticking to rollers/scorers, etc.) and consumption. Addition of emulsifiers such as glycerol monostearate or lecithin can reduce both hardness/brittleness and stickiness. Stickiness may also be reduced by coating the surface with dusting agents.

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Part III

Chocolate and Compound Coatings

Chocolate

15

15.1 Introduction

Of all confections, chocolate arguably has the longest history, having been already cultivated thousands of years ago in the reign of the Olmec. After Spanish explorers brought cocoa beans back to Europe, its usage slowly expanded. Used initially to create a drink, chocolate gradually developed into the smooth, creamy product we know today as a result of a series of technological advances. The history of chocolate cultivation and development has been the subject of numerous treatises (see, for example, Coe and Coe 2007).

The beginnings of the modern chocolate bar occurred in about the 1820s, when technological developments allowed modification of cocoa mass. For one, a method of separating cocoa butter from chocolate liquor was developed. Chocolate liquor, or ground cocoa nibs, with 50–60% cocoa butter, generally does not have enough fat to allow it to be turned into a chocolate bar. The addition of extra cocoa butter to chocolate liquor, though, allowed production of a sufficiently thin melted liquid chocolate that could be easily processed. Other developments, such as refining equipment for breaking down large particles and conches to smooth out flavors, were also needed. With these developments, modern chocolate was born – a smooth, creamy product with excellent eating properties.

Throughout the various countries of the world, there are many legal definitions of what is 'chocolate'. Chocolate standards are established by countries to provide rules regarding the formulation, the percentage and the types of ingredients that can go into a Standard of Identity product. In the United States, for example, the Standard of Identity for chocolate types is defined in the Code of Federal Regulations (CFR) title 21, part 161. Table 15.1 summarizes the main chocolate categories covered in the CFR. To be called chocolate, it must contain only certain ingredients in allowable ranges, as seen in Table 15.2. The most common types of chocolates seen are semi-sweet/bittersweet, sweet dark, milk, and white. In the United States, chocolate with 35% or more of chocolate liquor that meets the other legal criteria may be called semi-sweet or bittersweet chocolate (note that there is no legal definition of "dark" chocolate in the United States). However, traditionally and in many other parts of the world, bittersweet chocolate is reserved for products containing 50% or more chocolate liquor. Many different flavorings and spices can be added to chocolate, but in the United States, no flavorings can be added that imitate chocolate, milk or butter flavors. Emulsifying agents (generally soy lecithin or PGPR) are limited to 1% of the formula except for white chocolate where the level can be up to 1.5%. Other differences for white chocolate are that it is the only chocolate that allows for the addition of antioxidants (to prevent

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rancidity) and whey powder up to a maximum of 5%. White chocolate is also the only chocolate that has a maximum allowable level of nutritive sweetener (usually sucrose or lactose) at 55%. The CFR's allow only cocoa butter (cacao fat) or milk fat for the fat phase of chocolate. Other countries, however, allow up to 5% of certain vegetable fats within the legal specifications for chocolate. These fats provide the opportunity to moderate the properties of chocolate. Again, standards for chocolate products may differ around the world.

If any ingredient other than those allowed in the standards is added to chocolate, it cannot be called chocolate. Typically, these products are called compound coatings or confectionery coatings (see Chapter 16 for more details). However, many retail products have found creative names for compound coatings (chocolatey, fudgey, chocolate-flavored, etc.) to imply that the coating is made of real chocolate without actually calling it chocolate. The ingredient declaration for such products generally contains palm kernel oil as the primary fat in place of cocoa butter from chocolate mass.

Table 15.1 Types of chocolate covered by the United States Standard of Identity, Code of Federal Regulations (CFR)

Chocolate type	CFR[a]
Chocolate liquor	163.111
Cocoa powder (10–12% fat)	163.113
High fat cocoa (22–24%)	163.112
Sweet chocolate	163.123
White chocolate	163.124
Milk chocolate	163.130

[a] Chapter in Code of Federal Regulations

Besides making molded (solid or hollow) chocolate products, chocolate may be used in confections in a variety of ways. One popular way to utilize chocolate in a confection is in the candy bar (sometimes called a chocolate bar). Typically, the candy bar contains some variation of combinations of candy (nougat, caramel, etc.), at times with a wafer or cracker, all coated or enrobed in chocolate. The candy bar makes up a significant proportion of all confectionery sales. Chocolate is also used to coat fruits, nuts, or other centers in the process of chocolate panning (see Chapter 17). The properties of chocolate and its components determine how well a specific chocolate works in a specific confectionery application.

Stored under appropriate conditions, cool temperatures and low relative humidity, chocolate can last for well over a year without loss of quality. However, chocolate is a product that is not at true thermodynamic equilibrium and over time will physically change to reach a more complete equilibrium condition. In part, this change is due to the polymorphic nature of cocoa butter (Chapter 4) since the cocoa butter crystals in

Table 15.2 Standard of identity (US) for different chocolates

	Chocolate liquor	Semi-sweet (bittersweet) chocolate	Sweet chocolate	Milk chocolate	White chocolate
Cocoa butter	50–60%	–	–	–	Min 20%
Chocolate liquor (minimum)	100%	35%	15%	10%	–
Milk solids	–	<12%	<12%	Min 12%	Min 14%
Milk fat (minimum)	–	–	–	3.39%	3.50%
Sugar[a]	–	–	–	–	Max 55%
Emulsifiers	–	Max 1%	Max 1%	Max 1%	Max 1.5%
Antioxidants[b]	No	No	No	No	Yes
Whey products[c]	No	No	No	No	Max 5%

[a] Sugar – nutritive carbohydrate sweeteners

[b] Antioxidants – specified as α-tocopherol

[c] Whey products – whey cannot be included in milk solids calculations

chocolate are not in their most stable state. Thermodynamically, the cocoa butter crystals prefer to be in the most stable polymorphic state and if stored at inappropriate storage conditions (warm and cycling temperatures), will transform quite quickly. This polymorphic transition is associated with formation of bloom, or the white haze that develops on the surface (and at times, throughout the entire mass) of chocolate, although it should be noted that the polymorphic transition is a necessary event but not sufficient by itself to cause visual bloom. It has been shown that chocolate can contain the most stable cocoa butter polymorphic crystals without visual evidence of bloom (Bricknell and Hartel 1998). Details on storage of chocolate and bloom formation are given in Section 15.9.

This chapter is intended primarily to discuss chocolate as an ingredient in confections. More details on all aspects of chocolates can be found in Beckett (2009).

15.2 Cocoa Bean Production

The story of chocolate begins with the cacao tree, or *Theobroma cacao*. The cacao tree grows primarily in a narrow band 15–20° north and south of the equator. It prefers warm, humid environments with temperatures between 21 and 32 °C (70–90 °F), and abundant rainfall (1500–2000 mm per year). Since it grows best in shade, the cacao tree typically grows underneath a canopy of taller trees. The main cacao producing regions include West Africa (Ivory Coast, Ghana, Nigeria, Cameroon, etc.), Southeast Asia (Indonesia and Malaysia), and South/Central America (Brazil, Ecuador, Peru, Columbia, Mexico).

As with many plants, there are different varieties of cacao that produce quite different beans. Cacao has traditionally been grouped into three main cultivars: Criollo, Forastero and Trinitario. Each has quite different characteristics. Criollo beans are most highly valued since they are less bitter and more aromatic than other types of beans. However, the Criollo tree tends to be less robust, having a lower yield than other cacao tree species. Criollo beans make up less than 5% of the total cacao production, although it is the ancestral cocoa of the Maya and Aztec, growing in southern Mexico and throughout Central America. Forastero trees are a hardier tree, with higher yield because they are less susceptible to the numerous diseases and pests that can reduce cacao production. Despite the slightly more bitter bean produced, Forastero beans make up approximately 90% of world-wide cacao production. The Trinitario is a hybrid of Forastero and Criollo, making up the remaining approximately 5–10% of cacao production. Two other minor cultivars include Nacional, found in Ecuador, and Amelonada, found in central and northern South America.

With the advent of modern genotyping using molecular DNA sequencing, it appears that the classification of traditional cacao types is more complex. Motamayor et al. (2008), studying the genetic make-up of cacao trees in Latin America, suggest that there are ten clusters or groupings of cacao types, labeled Marañon, Curaray, Criollo, Iquitos, Nanay, Contamana, Amelonda, Purus, Nacional, and Guiana. Cacao genetics is an important topic of research, particularly as it relates to prevention of diseases and incorporation of insect resistance. Advances in cacao genetics will not only improve the yield and profitability of the cocoa farmer, but also improve the quality of cocoa beans for the chocolate producer.

Cacao pods develop from pollinated flowers and grow out of the trunks and lower branches of the tree. It takes about 180 days to go from pollination to pod ripening. Mature pods, which are about 15–25 cm (6–10 in.) long and 7.5–10 cm (3–4 in.) in diameter, typically contain 20–40 (sometimes up to 60) beans surrounded by a white mucilaginous pulp (see Figure 15.1). Once the pods have ripened on the tree, they are manually harvested and cut open, revealing the beans and pulp inside. The beans and adhering pulp are removed from the hull, which is discarded. The beans and the sweet acidic pulp are fermented for up to eight days, dried, bagged and transported for export or increasingly, into value added products locally. Fermented and dried beans may be processed into chocolate liquor, cocoa powder and cocoa butter within the coun-

Figure 15.1 Image of a cacao pod showing beans surrounded by mucilage (Courtesy of National Confectioner's Association)

try of origin, but it is still more common for them to be exported for further processing. The typical sequence of processing steps experienced by cocoa beans from harvest to shipping is provided in Figure 15.2.

15.2.1 Fermentation

One of the two most important steps in developing the desired chocolate flavors in a cocoa bean is fermentation (the other is roasting). Although a fermented bean itself does not yet have the expected chocolate flavor, without fermentation, a cocoa bean does not develop the desired flavor characteristics when roasted. Fermentation of the cocoa bean produces precursor molecules necessary for proper chocolate flavor development in subsequent steps, particularly roasting. Thus, it is important that fermentation be carried out properly since both under-fermentation and over-fermentation lead to poor flavor development during roasting. A variety of steps need to take place to ensure proper fermentation. Recent reviews by Thompson et al. (2013), de Vuyst and Weckx (2016), and de Melo Pereira et al. (2016) provide further details of the microbial aspects of fermentation while de Brito et al. (2000) covers structural and chemical changes in the cocoa bean.

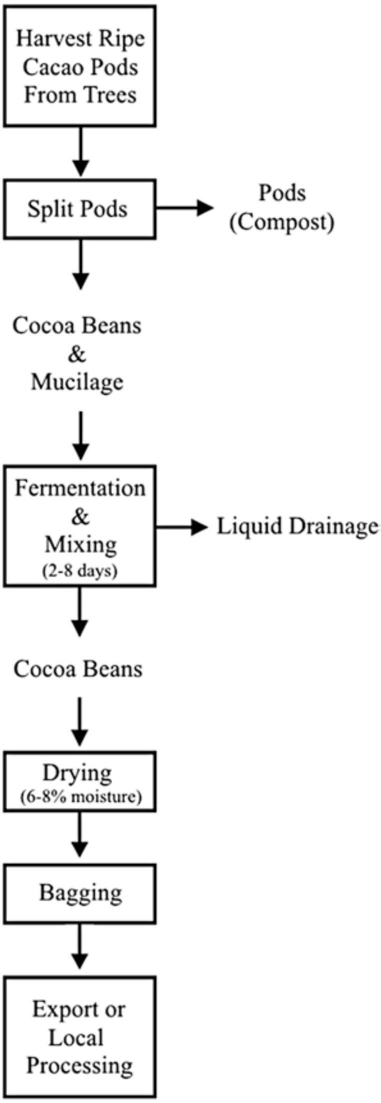

Figure 15.2 Typical processing steps for cocoa beans on the plantation

Fermentation generally involves piling beans with the attached mucilaginous pulp and then allowing natural fermentation processes to take place. The indigenous yeast and bacterial population break down the sugars and organic acids in the pulp. The beans may be heaped together and covered with leaves (banana or plantain) or piled into boxes with holes in the bottom to allow drainage. A sufficient mass of beans (sometimes up to hundreds of kilograms) is needed to ensure heat buildup during fermentation. Fermentation typically takes anywhere from 2 to 10 days, with Forastero beans requiring longer fermentation times than Criollo beans. Much of the fermentation process occurs under anaerobic conditions, although mixing of the beans occurs periodically, which adds oxygen and allows aerobic fermentation to occur as well. Fermentation must be carefully controlled since longer fermentation times (over-fermented beans) lead to excessive acidity as well as objectionable off flavors (e.g., musty or garbage-like flavors).

The chemical changes that occur during fermentation are quite complex and still not completely elucidated despite years of study. Numerous microbial species, including fungi, yeast, lactic acid bacteria and acetic acid bacteria, are involved in fermentation (Ardhana and Fleet 2003; Thompson et al. 2013). Numerous enzymatic reactions also take place during fermentation, with proteases, peptidases, invertase, polyphenol oxidase and glycosidases all contributing to the generation of flavor precursor molecules (Hansen et al. 1998).

In general, the fermentation process progresses through the following steps (Hancock 1998; Thompson et al. 2013; de Vuyst and Weckx 2016). First, yeasts convert sugars and citric acid in the pulp to ethanol and in the process, create anaerobic conditions. The maximum ethanol concentration may reach as high as 5–6%. Bacteria then convert ethanol first to malic and lactic acid, and then to acetic acid, CO_2 and water, with a final ethanol content of less than 1%. The process generates sufficient heat to warm the pile of beans to as high as 40 °C (104 °F) in the first day. Meanwhile, pulp pectinase activity breaks down the pulp, allowing water, sugars and acids to drain away. Lactic acid bacteria then produce lactic acid from the sugars, ethanol and citric acid while the acetic acid bacteria continue to make acetic acid from ethanol. Within the first few days, the beans have been killed by the heat, alcohol and acids generated during fermentation. Cell death and the associated physical changes in the first two days of fermentation allow enzymes and cell liquids to diffuse throughout the nib, allowing various reactions to occur. Also, the bacterial activity causes the temperature to further increase to about 50 °C (122 °F). Bacterial activity continues for the duration of fermentation with conditions becoming increasingly aerobic. pH changes occur during fermentation, with pH of the pulp increasing from about 3.8 initially to about 4.8 to 4.9 and pH of the bean decreasing from 6.3–6.5 to 5.0–5.1 (Ardhana and Fleet 2003; de Vuyst and Weckx 2016).

Numerous microorganisms are involved in cocoa bean fermentation, depending on the microbial flora within a certain region. Even plantations within the same country may have slightly different fermentation processes due to differences in the indigenous microflora (Thompson et al. 2013). Furthermore, different microbes are more prevalent in different stages of the process. The progress of a variety of different microorganisms during fermentation of cocoa beans in Indonesia has been documented (Ardhana and Fleet 2003). Several types of microorganisms increased substantially in number in the first day of fermentation but then began to decrease through the second and third days. These included filamentous fungi (*Penecillium citrinum* and an unidentified basidiomycete were dominant), and yeasts (in order of abundance: *Kloeckera sp., Saccharomyces cerevisiae* and *Candida tropicalis*). A wide range of other microorganisms also were enumerated, particularly in the early stages of fermentation, but their populations were minor compared to the above-mentioned species. Each of these species showed a similar increase in the first day of fermentation followed by a rapid decline to almost nothing after about 2–3 days. In contrast, *Bacillus* species grew continuously throughout fermentation and, with the decline of the other microbes, dominated the fermentation process over later stages. The specific *Bacillus* species in most abundance was different across the three different estates where the fermentation experiments were conducted. Clearly, this study shows the complexity of the fermentation process. To summarize, factors that affect fermentation of cocoa beans include (1) the nature of the local microflora, (2) the characteristics of the pulp (i.e., pH, water content, quantity, composition, etc.), and (3) fermentation conditions (i.e., temperature, time, frequency of turning to open the process to aerobic microorganisms, etc.).

Based on the wide spectrum of microorganisms present, it is no surprise that numerous enzyme reactions also take place during fermentation, particularly in the early stages where the greatest diversity of microorganisms exists. These enzyme reactions occur both in the mucilaginous pulp and the cotyledon (bean/nib) itself. The major enzymes active during fermentation include invertase, pectinases, proteinases, polyphenol oxidase, and glycosidases.

One of the most important enzyme activities for generation of flavor precursors is hydrolysis (inversion) of sucrose into the reducing sugars, glucose and fructose. These are both reactants in the Maillard browning process responsible for much of the chocolate flavor. In the pulp, inversion of sucrose by invertase and breakdown of pectin by pectinases cause the white mass to turn into a clear liquid that drains out of the bottom of the fermentation box. Invertase activity also occurs within the bean itself (cotyledon invertase), although its activity is significantly lower than the pulp invertase (Hansen et al. 1998). The sugars in both pulp and bean are continually used as substrate by the bacteria during fermentation.

Several different types of proteinases are active during cocoa bean fermentation. The initial step in protease activity involves an aspartic endoprotease, which hydrolyzes the globulin storage protein in the cocoa bean. Aminopeptidase and carboxypeptidase further break down the protein into peptides and individual amino acids, both of which are also necessary for the Maillard browning reaction.

The activity of polyphenol oxidase (PPO) during fermentation has taken on increasing importance in recent years as the healthful effects of polyphenols are explored. The flavanol, epicatechin, is the predominant polyphenol found in cocoa bean, with some estimates suggesting that total polyphenol content of raw beans is 12–18% on a dry bean basis (Kim and Keeney 1984; Payne et al. 2010). The epicatechin content of raw beans (freeze dried for analysis) was found to vary from about 35 to 43 mg/g defatted sample (Kim and Keeney 1984) or 12–16 mg/g whole dried bean (Payne et al. 2010). During fermentation, polyphenols undergo both enzymatic and nonenzymatic oxidation and condensation reactions. The result of these reactions is both loss of polyphenol content and generation of brown pigments. According to Kim and Keeney (1984), approximately 75–80% of the polyphenols are broken down during fermentation and drying, with much of that loss coming in the first day or two of fermentation. Payne et al. (2010), for example, found a decrease in epicatechin from 12.4 to 1.7 or 0.8 mg/g for Ivory Coast or Papua New Guinea beans, respectively, during typical fermentation processes (Ivory Coast: 4–5 days; Papua New Guinea: up to 10 days). In the same fermentation, catechin levels decreased from 0.46 to 0.08 or 0.05 mg/g, respectively, for the same beans. Clearly, there is a large decrease in flavonols, particularly epicatechin and catechin during fermentation. The ratio of epicatechin to catechin, thought to influence health effects, decreased from 29.3 in unfermented beans to 17.1–20.1 in fermented beans.

The epicatechin content of a sampling of fermented beans from around the world varied from 2.6 to 16.5 mg/g dry sample weight (Kim and Keeney 1984). Loureiro et al. (2017) summarized data on total phenol, catechin and epicatechin contents of various South American beans. Results varied widely with total phenolic content as low as 35 and as high as 204 mg/g and epicatchin from as low as 2.2 to as high as 17.2 mg/g. This variation arises in part due to the initial differences among cocoa beans, but also from differences in fermentation. Some beans received lighter fermentation conditions, and hence, less polyphenol loss, than others (Counet et al. 2004). Because of the health interests related to flavanols, new processes are being developed to enhance flavonoid content in cocoa products (Tomas-Barberan et al. 2007; de Vuyst and Weckx 2016).

Glycosidases are also active during fermentation of cocoa beans, hydrolyzing purple anthocyanidin pigments in the raw bean into cyanadins and sugars. This degradation leads to an initial bleaching effect; however, subsequent reactions of the enzyme degradation products lead to formation of tannins, and eventually to brown pigments.

Enzyme activity occurs throughout the fermentation process and is eventually deactivated during the drying stage. Note that typical enzyme reactions related to germination do not appear to be important during fermentation. This lack is attributed to the presence of a germination inhibitor in the pulp (and testa) and the lack of fat degradation during fermentation (Hansen et al. 1998).

15.2.2 Drying

Cocoa beans after fermentation need to be dried to about 6–8% to prevent problems during storage. Often, drying is accomplished by sun drying. The beans can be spread onto large, shallow trays, a tarp spread on the ground, a concrete slab or on raised bamboo slat drying platforms. The beans are left out in the sun to dry but are immediately covered in case of rain. Sun drying may take from a week to 2 weeks to ensure moisture content decreases to 7% or less. The beans are periodically raked to ensure that all beans are dried uniformly.

In regions where sun drying is not feasible, air dryers may be used. These generally involve some method of heating air and blowing warm air at 60–70 °C (140–158 °F) across the beans to promote drying. Dryer design, materials of construction, and heat source vary from region to region. In all designs, however, it is important that combustion products, particularly smoke from wood fires, do not come in contact with the beans as they dry lest undesirable smoky flavors be introduced.

The drying step, while primarily dedicated to removing moisture, also entails residual fermentation processes. Specifically, enzyme and microbiological reactions still occur during drying until either the water content is sufficiently reduced (less than 7%) and/or the enzymes are inactivated. For example, continued degradation of polyphenols occurs during drying, with the rate depending on temperature, moisture content and relative humidity (Kyi et al. 2005). Polyphenol oxidase reaction also contributes to browning of the bean during drying. Drying too rapidly can inactivate enzymes prematurely, with the result being less desirable flavor development when the beans are roasted.

Cocoa beans dried to 6–7% moisture are stable for transport and storage. If protected from moisture or infestation, dried beans can be stored for a year or more. Beans must also be stored away from sources of odor, such as rubber or petroleum fumes, and any other sources of volatiles since the beans are prone to picking up whatever odors are present in the storage area. For example, significant flavor changes will occur if dried cocoa beans are shipped in close proximity to crude rubber latex, which may also be grown in or around farms in Indonesia or Ivory Coast.

15.3 Cocoa Bean Composition and Quality Aspects

The specific composition of cocoa beans and quality attributes can vary widely, depending on the cacao varieties, environmental conditions during growth and postharvest processes. Table 15.3 shows the proximate composition of two varieties of raw cocoa beans. Raw beans contain 50–60% moisture and 20–25% fat. However, composition changes significantly due to processing steps. After fermentation and drying, the composition of the cocoa beans has changed considerably, as summarized in Table 15.4. More detailed reviews of cocoa bean composition are provided by Tran et al. (2015) and Loureiro et al. (2017). In most commercial chocolate manufac-

Table 15.3 Proximate composition (in weight %) of raw cocoa beans (Sotelo and Alvarez 1991)

	Criollo		Costarrica	
	Seed	Shell	Seed	Shell
Moisture	52.5	94.7	61.0	90.1
Protein	7.9	0.4	6.3	1.0
Fat	23.9	0.1	19.6	0.1
Carbohydrate	10.5	2.8	3.6	4.4
Fiber	3.1	1.5	3.2	3.4
Ash	2.1	0.5	1.4	1.0

Table 15.4 Composition (in weight %) of fermented and dried cocoa beans

	Nib		Shell	
	Minimum	Maximum	Minimum	Maximum
Moisture	2.3	3.2	3.7	6.6
Fat	48	57	1.7	5.9
Protein[a]	2.2	2.5	1.7	3.2
Starch	6.5	9	3.4	5.2
Fiber	2.2	3.2	12.8	19.2
Ash	2.6	4.2	7.1	20.7

After Minifie (1989)

[a] Measured as total nitrogen

turing plants, cocoa beans are the starting point for making chocolate.

Incoming cocoa beans are inspected for insect infestation, presence of mold, degree of fermentation, fat percentage of the nib, percentage of nib versus shell, size of the bean, and amount of foreign material. Typical dried cocoa beans have approximate composition of 80% nib, 12.5% shell, and 7.5% moisture. The weight of an individual cocoa bean is approximately 1 g. Larger beans have a higher fat content while small beans (and especially those that are shriveled) have a higher shell content. Smaller beans are also more difficult to process.

The quality of bean fermentation, presence of mold or insect infestation can be determined by doing a ‘cut’ test. In this test, 100 cocoa beans (generally) are sliced vertically and evaluated. Cocoa beans with no fermentation have a slaty/gray color while well fermented beans have a brown color. Purple color of cut beans is associated with partial fermentation while over-fermented beans have a dark brown or in some cases a pale-yellow brown color (Minifie 1989). The degree of bean fermentation will greatly affect the flavor of the final chocolate products that are made.

In addition to a cut test and various analytical tests, the cocoa beans are evaluated for flavor. A small sample of the beans are roasted and after the shell is removed, the nibs are ground into chocolate liquor, which is then evaluated by a trained, expert taste panel. The chocolate liquor flavor should be clean without flavors of mold, smoke, excess acidity or other defects. All of these tests are done to insure a consistent finished chocolate product.

Table 15.5 Typical composition of chocolate liquor

Component	Composition (g/100 g)
Moisture	1.0
Fat	55.0
Protein	11.9
Sugars	0.5
Starch	6.5
Fiber	16.6
Ash	3.1
Organic acids	2.1
Theobromine	1.1
Caffeine	0.1

From De Zaan Cocoa Manual (2009)

After cocoa beans have been roasted and ground into chocolate liquor (see next section for details), further changes in composition are expected. Again, the composition of chocolate liquor is dependent on all the factors noted previously and thus, it is difficult to specify its exact composition. Table 15.5 provides a representative composition for chocolate liquor (De Zaan Cocoa Manual 2009). The mineral content of chocolate liquor includes potassium (1%), phosphorous (0.4%). magnesium (0.3%), calcium (0.08%) and small amounts of sodium, chloride, iron, zinc and copper (De Zaan Cocoa Manual 2009). Organic acids found in chocolate liquor include acetic, citric, oxalic and malic acids (Luna et al. 2002). Accordingly, the pH of dried cocoa beans and chocolate liquor vary with country of origin and processing. Cured cocoa beans have pH values that vary from as low as 4.7 to as high as 5.6 (Jinap and Dimick 1990), whereas chocolate liquors from Ecuadorian cocoa had a pH range from 5.6 to 6.3 (Luna et al. 2002).

The alkaloid content of chocolate is of particular interest. Zoumas et al. (1980) analyzed 22 samples of chocolate liquor from various origins and found an average of 1.22% theobromine (range: 0.82–1.73%) and 0.214% caffeine (range: 0.062–0.416%). The average ratio of theobromine to caffeine was 7.9, but that varied from as low as 2.5 to a high of 23.0. These two methylxanthine components are responsible for many of the reputed effects of chocolate, including a pleasant sense of well-being.

The polyphenol content of chocolate has gotten increasing attention recently. The main polyphenols in cocoa include catechins, proanthocyanidins and anthocyanins, although the exact composition depends on species and country of origin. Raw beans contain about 15% polyphenols on a dry, fat-free basis, although that can vary based on growing region and variety. See Section 15.8.2 for more details on polyphenol content in chocolate products and their fate during processing.

15.4 Chocolate Processing

Once fermentation and drying have been completed, the beans are shipped to a processing facility where they undergo various processing steps in their conversion into chocolate and other related products. What happens to the beans in the manufacturing facility (flavor, fineness, viscosity, etc.) determines its use in the confectionery, bakery, ice cream, and other industries.

The general steps for converting cocoa beans into chocolate confections are outlined in Figure 15.3. Although the order of these steps may vary somewhat from plant to plant, the general approach is basically similar in all chocolate manufacturing plants. Briefly, the beans must be cleaned prior to roasting and removing shells to leave the cocoa nib, the center part of the cocoa bean. The nib is ground into chocolate liquor. Either the nib or the chocolate liquor may be treated with alkali (Dutch processing). A portion of the liquor is pressed to remove cocoa butter, leaving behind cocoa powder (typically 10–12% fat). To make chocolate, the main ingredients, chocolate liquor, sugar, cocoa butter and other ingredients (i.e., milk powder, milk fat, etc.), are mixed together, refined to reduce particle size, conched to smooth flavors, and standardized to the specified viscosity. Prior to use, the liquid chocolate must first be tempered to seed cocoa butter crystallization before forming (i.e., molding, enrobing, dipping, etc.) to make chocolate bars or enrobed confections.

15.4.1 Cleaning and Sorting

Coming from the plantation, cocoa beans are a typical agricultural raw material that must be cleaned prior to use. They can bring with them substantial amounts of materials that must be removed, including such foreign material as dirt, stones, string, glass and metal. Also removed in the cleaning process is cocoa bean related material that includes cacao husk, flat beans, and clusters of beans. All of this material must be removed to avoid off flavors and contamination in the chocolate.

A screen or sieve is first used to separate extraneous materials by size. Lighter materials (dust, sand, string, husks, sticks, etc.) are removed with counter-current air sifters. The beans then pass through a magnetic device to remove iron parts. Electromagnetic induction units are needed to remove nonmagnetic metals like stainless steel. Stones can be removed using an air separator, where lighter cocoa beans are separated from the heavier denser stones with a fluidizing flow of air.

15.4.2 Winnowing

Cocoa beans are made up of the nib (≈85%) and the shell (≈15%). Winnowing is the process of separating the shell from the cocoa bean center, also known as the nib. The object is to have complete cracking of each and every bean followed by complete separation of shell. In the United States, removal of the shell is required by law

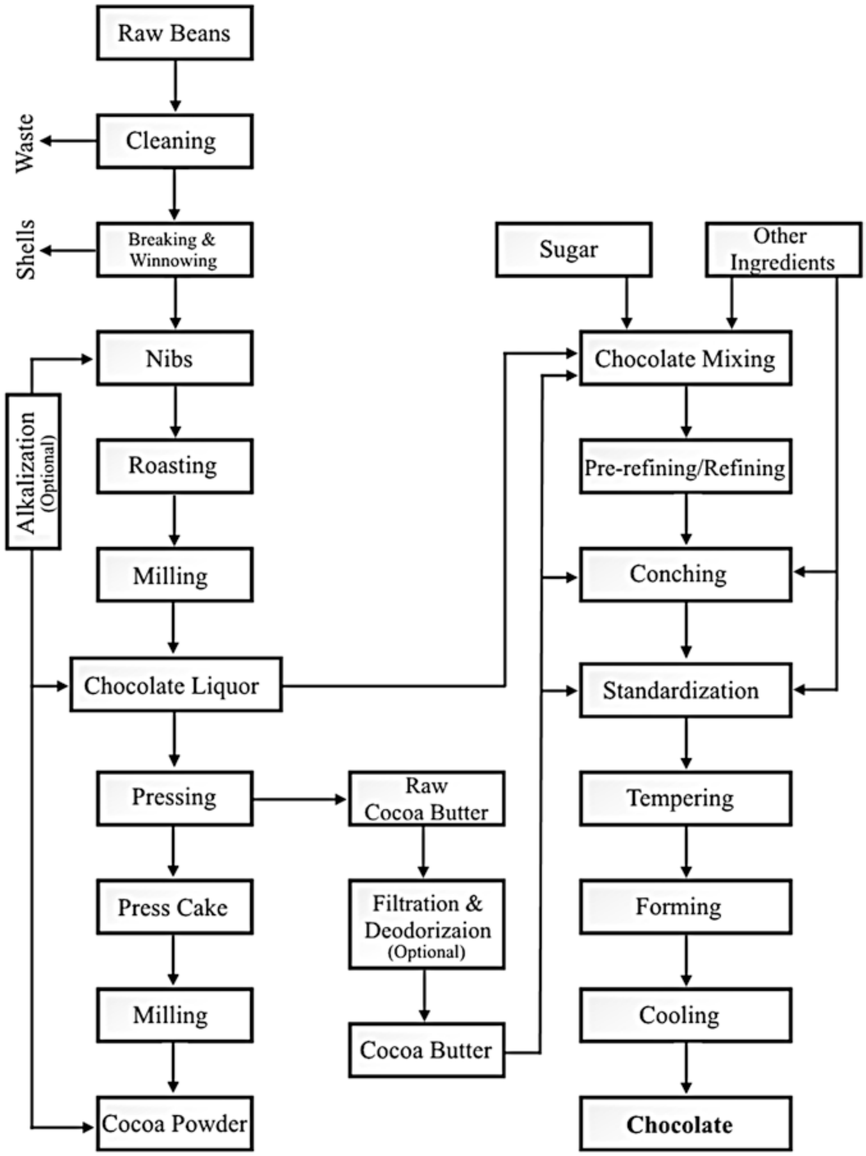

Figure 15.3 Typical processing steps for converting cocoa beans into chocolate for use in confections

and there cannot be more than 1.75% of shell in the resultant chocolate liquor. Inclusion of the shell in chocolate can lead to introduction of off-flavors, increase wear of refining equipment, higher microbiological counts and due to its fibrous nature, the shell also makes processing downstream less efficient.

Winnowing may be done either before or after roasting and is generally accomplished by crushing the beans to release the shell and then separating the lighter shell material from the nibs with an air classifier. Crushers may be either centrifugal, where the beans are ejected out of a spinning disk to impact a breaker plate, or reflex crushers, where the beans pass through two metal rollers that mechanically crack them.

Pretreatment of the beans is often necessary to ensure more efficient winnowing and is usually done with nib roasting. This may include infrared, thermal or steam pretreatment. Steam pretreatment is also used as a process to reduce the microbial load in the chocolate liquor.

Smaller beans require more force to break than large ones and increase the losses in the winnowing step. During this process, efficiencies are increased when all of the beans in a lot are of uniform size. New winnowing technologies coupled with better pretreatments are continually being developed to minimize nib losses and optimize shell separation.

15.4.3 Alkalization (Dutching)

Cocoa beans after fermentation and drying have a low pH as a result of the acetic acid generated during fermentation. The pH of dried beans generally falls in the range from 4.7 to 5.5, although pH as high as 6.3 have been found (Loureiro et al. 2017). Raising the pH through alkalization causes significant color change in the finished chocolate. Colors can range from dark brown to a reddish hue to black. By neutralizing some of the acids, alkalization also changes the flavor of the chocolate, generally making it less bitter with more of a 'brownie' type note. This flavor change arises in part because the pathway of the Maillard browning reaction depends on pH. Alkalization also enhances the ability of the resulting cocoa powder to disperse in water, making Dutched cocoas well suited for use in chocolate milk.

Either nibs, chocolate liquor or cocoa powder can be alkalized, with each giving its own unique color and flavor. Alkalizing nibs and chocolate liquor can significantly affect the cocoa butter flavor and require deodorization to have a final neutral flavor. Alkalization may be done in a batch reaction vessel or continuously in a screw conveyor. Color change from alkalization is influenced by such factors as the concentration and type of the alkali solution, pressure, time and temperature. According to the United States Code of Federal Regulations (21CFR163.110), the permitted alkalization agents in the United States are ammonium, potassium or sodium bicarbonate, carbonate or hydroxide. Also permitted is magnesium carbonate or oxide. The maximum permitted levels of alkalization agents are 3 parts potassium carbonate to 100 parts cocoa nibs.

15.4.4 Roasting

Cocoa beans and nibs (and to a lesser extent chocolate liquor) are roasted to bring out the flavor changes associated with chocolate and to reduce the microbiological count. Fermented cocoa beans contain very high microbial counts, some of which may be pathogenic. Thus, it is critical that microbial counts be reduced as close to zero as possible and that all pathogens are completely killed.

Heating cocoa beans to 120–140 °C (248–284 °F) destroys microorganisms and causes significant, mostly desirable, changes in composition. The roasting step is where much of the cocoa flavor is developed, primarily through the Maillard browning reaction, in addition to a reduction in water and acid content. Thus, it is important to control the roasting process carefully to ensure proper chocolate flavor development.

Whole beans can be roasted prior to winnowing since the roasting step helps release shell from nib. However, it is now more common for the nibs to be roasted separately, after winnowing and shell removal.

Roasters can be either batch or continuous, with a variety of heat transfer mechanisms at work, although a flow of hot air is the still the primary heating mechanism. The drum roaster is one of the oldest and simplest roasters; it can be used for either nibs or whole beans. The beans or nibs are loaded into the drum (sometimes with water or even sugars added to moderate the flavor reactions) and exposed to hot air as the drum turns. Specific roasting profiles can be employed by changing the temperature of the input air and/or the time of roasting. After roasting is complete, the beans are removed from the drum for cooling. Large continuous roasters can be cylindrical drums that rotate slowly, turning the beans over as hot air passes through the tumbling bed of beans. Raw beans enter one end of the drum and work their way slowly to the exit, passing through several sections where temperature can be independently controlled. The residence time in the drum, which is governed by the speed of rotation and the downward angle of the drum, is controlled to ensure proper roasting of beans at the exit. Other continuous roasters use a counter-current flow of air to heat the beans, which fall through the roasting chamber either on a series of shelves or trays. Lower sections of the vertical roaster can be used for cooling with a separate flow of air. One vertical roaster simply controls downward cocoa bean movement with a discharge roll to control dwell time, while hot air roasts the beans (Figure 15.4). Multiple heating or cooling zones are possible in this system. After roasting, the beans or nibs must be cooled before further processing.

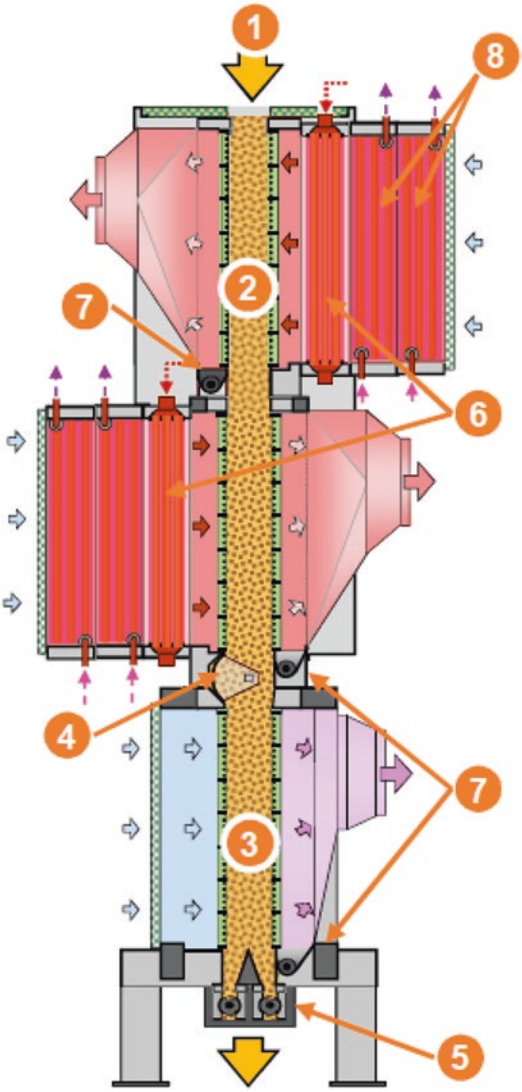

Figure 15.4 Vertical bean roasting system. *1* product inlet; *2* roasting zone duct; *3* cooling zone duct; *4* central slide gate; *5* discharge roll for roasted cocoa beans; *6* air heater element; *7* dust discharge to bin; *8* two air heating element for heat recovery system (Courtesy of Bühler)

Another option is to roast the chocolate liquor. In this process, nibs are ground into chocolate liquor prior to roasting. Liquor roasting is usually accomplished by forming a thin film of the liquor or sprayed droplets exposed to hot air. Thin-film roasters may use either falling-film or rising-film technology to create a large surface area for exposure to hot air during roasting. Water and/or sugars may be added to the chocolate liquor prior to roasting to modify flavor development. A vacuum may be applied to the thin layer or drops of liquor to help remove off-flavors.

Based on how cocoa beans are handled and processed in the producing countries, beans typically have a fairly high microbial population. Roasting of the beans, nibs or liquor will reduce this count and is often considered a critical control point for the processor in meeting safety/sanitation standards. The reduction in count is governed by the amount of moisture present (more moisture makes for an easier 'kill' step), the time and temperature of the roast, and the initial microbical load. Some products and processes require further reduction in the microbiological load. This can be accomplished by sterilization (or debacterization), either before or after roasting. Debacterization is done with steam since the combination of heat and moisture penetration into the surface of the bean is required to destroy bacteria. This process also helps separate shell from bean, making the winnowing process easier.

15.4.5 Nib Grinding

Cocoa nibs are ground into chocolate liquor after roasting and prior to addition of other ingredients to make chocolate. Turning nibs into chocolate liquor requires some method of breaking and grinding the bean into small particle size to break the cell structure and free the entrapped cocoa butter. Optimal grinding of nibs requires less than 2% moisture content, and warm temperatures to ensure the cocoa butter is melted. Grinding nibs into chocolate liquor requires multiple steps – coarse, intermediate and fine grinding. The end result of nib grinding should be a smooth, free-flowing chocolate liquor.

Numerous methods have been developed and used for grinding nibs into liquor. The original stone mills used for coarse grinding of nibs have largely been replaced by impact mills, which are more efficient and give better control over particle size reduction. The beater blade mill, with either knives, blades or hammers, generates a high-speed impact to break the nibs into smaller pieces, which are then forced through a sieve to ensure particle size reduction. The next stages of grinding can be done in a variety of mills, including roll refiners, stone mills, or ball mills. In a stone mill, nibs are ground between two stone discs, one rotating and the other stationary. Often, triple stone mills are used that have three sequential pairs of stones to grind the nibs in three stages. Ball mill refiners, whether horizontal or vertical, are common for grinding nibs to reduce particle size. Ball mills utilize grinding media (balls) to help reduce particle size. The coarse liquor enters the vertical ball mill at the bottom and is pumped up to a sieve at the top that only allows liquids and small particles through. As the liquor traverses the mill volume, the cocoa particles are broken down by shear and impact forces due to the motion of the steel balls as they are agitated by the mixer. The mixing shaft may be outfitted with pins or disks. To ensure efficient grinding operations, a series of two or three mills may be used with steel ball size decreasing from 15 to 2–5 mm.

The final particle size distribution for grinding depends on whether the cocoa mass is intended for pressing to make cocoa butter or if it will be used directly in chocolate manufacture. For pressing cocoa butter, particle size of cocoa mass should be relatively large, about 50 μm (as measured by micrometer). The large mean size allows more efficient extraction of the cocoa butter. Relatively few particles should be less than 20 μm, since small particles can easily plug filters during pressing. Chocolate liquor intended for the manufacture of chocolate generally has a particle size reduction to that of the finished chocolate, about 20 μm. This reduces the wear of the roll refiners and allows the chocolate liquor to be added directly to the mass in the conche, if needed.

15.4.6 Cocoa Butter and Cocoa Powder Production

Chocolate liquor yields cocoa powder and cocoa butter upon pressing. Separation of the two components of cocoa nibs is usually accomplished in a filter press, but may also be done by an expeller press. In some rare cases, cocoa butter may be removed by solvent extraction in order to produce a cocoa powder with 0–2% residual cocoa butter. The nature of the cocoa butter produced (composition and solidification properties) is different for each extraction process as is the cocoa powder remaining. Thus, the desired characteristics of both cocoa butter and powder determine which separation method is preferred.

Typically, the highest quality cocoa butter and powder are obtained by high pressure filter press. Here, the fluid liquor at a temperature of about 100 °C (212 °F) is pumped under pressure into a plate-and-frame type filter press where the liquid cocoa butter is pressed out of the mass. In the filter press, cocoa particles are retained by a metal mesh screen while the liquid cocoa butter passes through when hydraulic pressures of 41.4–82.8 MPa (6000–12,000 psi) are applied through the hydraulic ram. Cocoa butter passing through the filter is collected and pumped through a filter into a holding vessel. Once compression is complete, the ram is released, opening the filter pots and allowing the press cake to be released for subsequent grinding. Efficiency of pressing depends on such parameters as liquor temperature, moisture content, degree of roast, particle size, pressing time and pressure applied at the press. Moisture content should be low, less than 1 to 1.5%, with a uniform distribution of moisture throughout the liquor. Homogenization of liquor may be recommended in certain cases to ensure efficient filtration. Particle size of the cocoa liquor is critical to efficient filtration. The particles must be small enough to allow separation of cocoa butter from the cell wall structure, but not so fine that they plug filters and decrease the efficiency of the press operation. Careful control of operating variables allows separation of a high-quality cocoa butter containing few impurities. The cake is pressed to the desired fat content determined by the end product uses and applications. Most common is 10/12 cocoa powder (10–12% fat) followed by 22/24 cocoa powder (22–24% fat).

Cocoa butter may sometimes be separated from whole beans or other winnowing products (nib dust, small nibs, etc.) in an expeller press, a process used widely for separating oil from oil seeds. Here, a rotating screw forces beans at 50–60 °C (122–140° F) against the wall of a tapering cone shell with slits in the wall to allow liquid oil to pass through. The combination of shear forces and applied pressure as the beans are compressed into a smaller and smaller space forces the liquid cocoa butter out of the cellular structure of the beans. Cocoa butter is collected as it exits the wall of the expeller and is pumped into a holding tank. The defatted cocoa mass exits the cone end of the expeller and is removed for further processing. The beans are often pre-treated with steam to soften them and allow easier removal of the fat through the shearing process in the expeller. Expeller cocoa butter generally contains fine cocoa particles that must be removed by further filtration. The expeller cake is ground and used as cocoa powder for certain applications; however, the properties of expeller-produced cocoa powder may be different from that produced in a filter press due to the shearing nature of the forces. Expeller-based cocoa powder generally absorbs more liquids and fats than hydraulically pressed powder.

While not common, cocoa butter may also be extracted from beans or pressed (filter or expeller) cocoa mass by use of organic solvents such as hexane to produce low fat cocoa powder. Either semi-continuous (e.g., a series of batch tanks) or continuous processes may be used for solvent extraction. In continuous plants, counter-current operation is employed, with solvent moving in one direction and the cocoa mass or beans moving in the opposite direction. As the hexane passes through the cocoa mass, it dissolves the cocoa butter and drains out of the defatted mass. Hexane-extracted cocoa butter must be treated to remove residual hexane and any other impurities removed by the extraction. Residual hexane must be removed from the cocoa powder as well. Solvent-extracted cocoa butter typically goes through a standard oil refining operation, including degumming, bleaching and deodorizing to produce a mildly-flavored cocoa butter.

The residual fat content of the cocoa cake influences the subsequent grinding process. Since the pressure in the filter has compressed the cocoa particles, with whatever cocoa butter remains, into a compact mass of aggregated particles, it is necessary to grind the cocoa cake in order to produce a fine cocoa powder. The first step in grinding is to break apart the compacted cake, usually by passing it between a set of rollers with intermeshing teeth. This creates a kibble, or lumps of press cake on the order of half a centimeter or so in size. Break down of this kibble is completed in impact mills, such as a hammer mill, air classification mill or a pin mill. The ideal end point of grinding would be the initial size distribution of the chocolate liquor fed into the press. It is unlikely that grinding of the press cake breaks down the initial particles any further, although it is likely that some aggregated particles remain in the ground cocoa powder. To aid in grinding, the kibble cake should be cooled to prevent a buildup in the mills. Cocoa powder is cooled in stages prior to packaging and storage. Proper solidification of the remaining cocoa butter in the powder is essential to prevent caking.

The quality of cocoa powder is dependent on the quality of the chocolate liquor used in its production and the processing steps for preparation. Typical composition of cocoa powder is given in Table 15.6. Besides fat content and particle size,

Table 15.6 Typical composition of cocoa powder

		Alkalized		
	Natural	1	2	3
Moisture (%)	3.0	3.5	3.5	4.3
Cocoa butter (%)	11.0	10.0	23.5	21.5
pH[a]	5.7	7.1	6.7	6.8
Ash (%)	5.5	8.5	6.3	7.7
Phosphate[b] (%)	1.9	1.9	1.4	2.0
Chloride[c] (%)	0.04	0.9	0.7	1.1
Shell[d] (%)	1.4	1.0	0.5	1.0
Protein[e] (%)	21.2	18.7	17.5	18.7
Theobromine (%)	2.8	2.7	2.3	2.3

From Minifie (1989)

[a] In 10% suspension

[b] As P_2O_5

[c] As NaCl

[d] Calculated to unalkalized nib

[e] From total nitrogen corrected for alkaloids

other important quality parameters include pH (5.0–8.2), water content (4.5% maximum), color and flavor (depending on bean source, alkalization, etc.), and microbial content. Cocoa powder should be free of pathogens and will generally have a total microbial ranging from 1000 to 25,000 cfu/g depending on specifications and final application.

15.4.7 Milk Processing for Chocolate

The milk from cows contains about 88% water and, as such, is unsuitable for mixing with chocolate. The majority of the water must be removed from milk in order to make it appropriate to add to chocolate liquor and sugar for production of milk chocolate. Traditionally, two main processes are used for processing milk for use in chocolate – dried powder (either skim or whole milk) and milk crumb.

15.4.7.1 Milk Powders

Dried milk powder is the most common ingredient used in the manufacture of milk chocolate. The majority of the powder used is spray dried, although some powder is also produced by roller drying. Milk powder may be made either from whole milk or skim milk. In spray drying, the milk (whole or skim) is atomized through a spray nozzle usually at the top of a drying tower where it comes in contact with warm air. The hot, dry air causes rapid evaporation of water from the small (less than 100 μm) droplets such that drying is complete within a minute or so in the drying tower. Dried powder is removed from the bottom and separated for further processing and packaging. The powder is a mixture of semi-spherical particles, often with internal cavities where super-heated fluid inner product has burst through a solidified (or case-hardened) shell. Dryer conditions determine the characteristics of the milk powder, particularly its residual moisture content. Chocolate processors specify high or (more commonly) low heat milk powders. High heat powders have more of a ‘cooked’ milk flavor and a lower whey protein nitrogen index (WPNI), a measure of the amount of undenatured whey proteins.

While less common, milk may also be dried on a roller dryer. Here, the milk is dried in a thin layer on a rotating cylindrical drum (a roller) with steam heating inside the drum. Heat transfer through the metal drum wall causes rapid evaporation of water from the milk layer out into the air around the roller. The dried milk layer is scraped off the drum as it rotates around and the powder collected for further processing and packaging. Because of the high temperatures, roller dried milk powder, whether skim or whole, receives higher heat treatment and typically has a much higher cooked-milk flavor than spray dried powder.

One parameter of importance when mixing dried milk powder into chocolate is the so-called free fat. Free fat is defined as the fat that is easily removed from the powder and is free to interact with cocoa butter. Spray drying, a technique often used as an encapsulation method because of the glassy matrix formed, has low free fat since much of the milk fat is tightly enclosed within the lactose/protein matrix. Even upon breakage in the refining operation (see Section 15.4.8), very little of the milk fat is released to interact freely with cocoa butter. In contrast, roller dried whole milk powder has particles that are more flat, with significantly more of the milk fat globules exposed at the surface. Although this makes roller dried whole milk powder more prone to lipid oxidation, the higher free fat level also means that almost all of the milk fat is free to interact with cocoa butter in milk chocolate. This provides a viscosity reduction not seen with spray-dried whole milk powder and also a softer textured milk chocolate. Also, since milk fat provides some measure of bloom inhibition in milk chocolate, higher free fat is seen as a positive aspect of roller dried milk powder. However, since spray dried milk powder is more readily available, some milk chocolate manufacturers choose to use spray dried skim milk powder (which also is not prone to lipid oxidation) and add anhydrous milk fat separately so that the entire amount of milk fat is able to interact with cocoa butter. Skim milk powder with anhydrous milk fat will give a much softer chocolate than one made with whole milk powder because of the eutectic phase behavior between milk fat and cocoa butter (see Section 4.3.2.3).

15.4.7.2 Milk Crumb

Production of milk crumb is an alternative to adding milk powder to produce milk chocolate. In fact, the milk crumb process was the original method, developed by Daniel Peter in the 1870s, to make milk chocolate.

Milk crumb is manufactured by heating milk, sugar and chocolate liquor together to produce a paste with about 10% water content followed by drying, often under vacuum, to final water content of about 1%. The original process of making milk crumb from milk first started by making sweetened condensed milk. Here, sucrose is added to milk as the water is evaporated off to reach about 12% moisture, where the sucrose is supersaturated and crystallizes to form numerous small crystals. Chocolate liquor is added at this point and the mixture is kneaded to form a semi-crystalline paste containing about 10% moisture, which then is dried under vacuum to a final moisture content of about 1%. This crumb is crushed to reduce size before being used to make milk chocolate. These steps were traditionally done in a batch process, but modern crumb equipment uses either a series of unit operations (rapid evaporation, drying) or a single unit combined mixer/dryer to accomplish crumb manufacture in a continuous process.

Of particular importance in milk crumb is the unique difference in flavor profile compared to dried milk powders. Specifically, cooking milk and sugar to high temperature and low moisture is the basis for making caramel (see Chapter 7) and thus, Maillard browning products contribute strongly to the characteristic flavor of milk crumb. In this case, the primary reducing sugar present is lactose with the protein components including both milk and cocoa proteins, giving a somewhat caramel-like flavor due to the effects of the Maillard reaction. Milk crumb flavor is further moderated through the addition of chocolate liquor to the mixture. The specific flavors generated in the milk crumb process depend on moisture content, temperature and the time at each stage, with temperature and time being the primary determinants in flavor production. Further details of flavor development in milk crumb can be found in Wells (2009).

Milk crumb is a highly crystallized, aerated matrix containing cocoa particles, small sucrose and lactose crystals, and air cells distributed in an amorphous phase of water, dissolved sugars, milk salts and proteins. The air cells arise from vacuum evaporation of water as the crumb is dried. The fat (both milk fat and cocoa butter) is distributed as small droplets throughout the matrix, which, ideally, release the fat upon refining to contribute to the continuous phase of the chocolate. If drying is too rapid, the crumb matrix can become glassy, limiting the release of fat during chocolate manufacture. As with milk powder, milk crumb dried on a roller-drier contains a substantial portion of free fat that is easily released to mix with the main cocoa butter phase in chocolate.

15.4.8 Mixing and Refining of Chocolate Mass

Following the individual preparation of chocolate liquor and cocoa butter, and whatever milk product will be added for milk chocolate, the ingredients must be mixed together for chocolate production. The sugar, chocolate liquor, and milk ingredient (if used) are added together with a portion of the cocoa butter for refining. A minimal amount of lecithin may also be added at this step to obtain the desired texture to feed the refiner rolls, but the bulk of lecithin is added in the conche.

Mixing of chocolate ingredients can be either a batch or continuous process. In the older batch process, each of the ingredients would be weighed into a mixing tank that provided adequate shear to bring the batch together into a uniform paste.

In continuous mixing devices, each ingredient is carefully metered into the mixer where mixing arms work or knead the materials to produce a homogeneous chocolate paste. The mass exiting the mixer is grainy (large particle size) with a paste consistency that is firm enough to pass through the pre-refiner rollers.

Particle size reduction, or refining, typically takes place in the 5-roll refiner. When operating correctly, the five-roll refiner efficiently reduces particle size of the chocolate mass to the desired size. However, a single five-roll refiner can decrease particle size only on the order of magnitude of five to ten times, meaning that to obtain a consistent 15–20 μm (micron) particle size after refining, the initial feed must have a particle size between 100 and 150 μm. For this reason, it is common to use a pre-refiner to do some preliminary particle size reduction and ensure a consistent feed material to the five roll refiner. A two-roll pre-refiner may be used to reduce particle size to about 100–150 μm. The pre-refiner can also eliminate the need for a separate pulverization step for sugar.

In a five-roll refiner, the chocolate mass first passes through the fixed gap between rollers 1 and 2. The gap spacing in the following rollers progressively decreases to produce the small particles necessary for chocolate. The bottom roller is slightly offset from the other four rollers, which are arranged vertically. The first gap is approximately 70–100 μm, with gap width decreasing sequentially to approximately 20 μm for the final gap, as seen in Figure 15.5. To ensure that the chocolate paste transfers from one roller to the next, the rotational speed of the rollers increases as the chocolate passes from the bottom to the top. That is, the bottom roller rotates at considerably lower RPM than the upper roller, varying from about 60 RPM on the feed roller to about 380 RPM on the top roller. Ground chocolate paste is scraped off the top roller, at which point it is ready to be conveyed to the conche.

The rollers are made of precision-ground, hardened stainless steel with a slight crown so that when under pressure in the refiner, a flat layer of chocolate paste with uniform thickness is spread across the entire length of the roller. The gaps between the rollers are set by applying hydraulic pressure to the top and bottom rollers. Each roller has cooling water circulating within to maintain the desired temperature since the frictional heat as the mass passes between two rollers can raise the temperature considerably. Proper roll temperature will also help the transfer of the chocolate paste to the next roll and maintain a uniform sheet on the rolls.

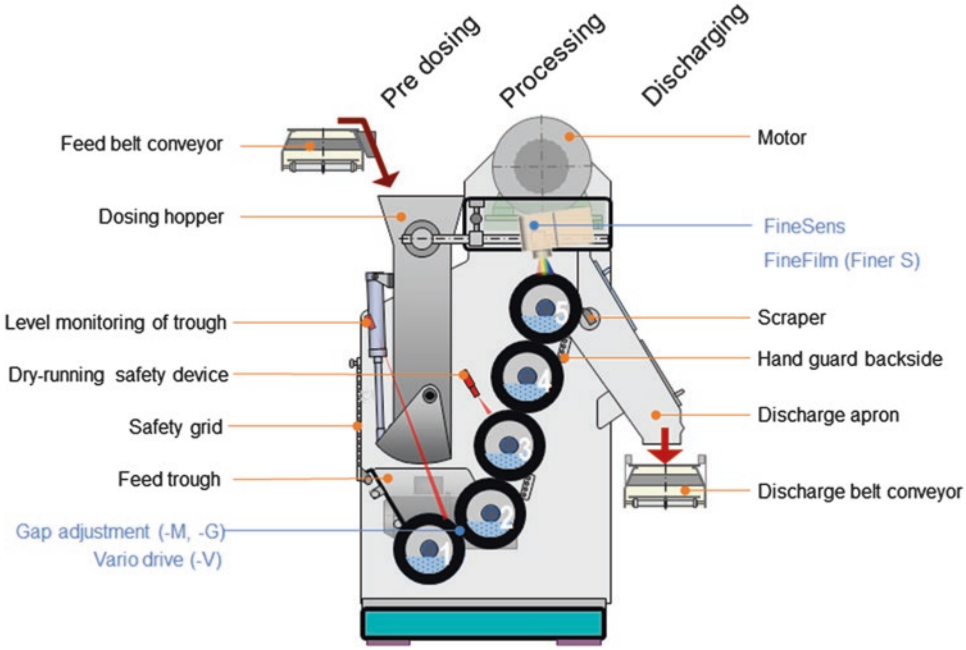

Figure 15.5 Cut-away of a typical five-roll refiner (Courtesy of Bühler)

Particle size reduction in a roll refiner occurs due to a combination of compression and shear forces. The different types of particles found in chocolate (sugar crystals, cocoa solids, milk powder or crumb) respond differently to these forces and break down in different ways. Depending on the brittleness (or ductility) of the particle, it may either fracture into multiple pieces or simply chip or abrade away the surface as particle size is reduced. The different breakage mechanisms have significant ramifications on chocolate rheology since the smallest abraded particles, with high surface area, require coating with a substantial amount of cocoa butter. Assuming that cocoa grinding has been completed prior to mixing the chocolate mass, the main task of the roll refiner is to reduce particle size of sugar crystals and the milk ingredient. Sugar crystals are typically quite brittle and thus, chipping, crushing and abrasion occur. This produces numerous fine particles, many of which may be sub-micron in size. Breakage of milk powders depends to some extent on refining temperature and whether or not the lactose is glassy or not. When the milk powder is glassy, it breaks as a brittle material. When refining temperature exceeds the glass transition temperature of the lactose matrix, the particles become more ductile, making it harder to grind. Furthermore, the powder surfaces become sticky when temperature is above the glass transition temperature, leading to a tendency to aggregate after the refiner.

The so-called "universal" chocolate system, or refiner-conche, may be used for particle size reduction in chocolate (Beckett 1994). In fact, this system accomplishes much more; it simultaneously grinds, blends, warms, refines, and conches the chocolate mass. The particles in the chocolate mass are broken as they are forced between rotating, spring-loaded blades that press against the inner wall of the cylinder. The process also allows release of water and volatiles, a function typically accomplished during conching. Since the refiner-conche tends to give a broader particle size distribution than the five-roll refiner, it may be used in conjunction with a ball mill for efficient refining (Beckett 1994).

An alternative method for producing refined chocolate paste for conching is to grind the individual components separately and then blend them together at the appropriate ratios. For example, sugar and the dried milk ingredient may be reduced in size to less than 30 μm in a classifier mill. This type of mill grinds particles on a milling disk with hammers, wedges or pins to break or fragment particles. A flow of air carries the smaller particles, with the desired size, through slits in a rotating cylinder to be collected in cyclones or a bag filter. Particles that are too large do not make it through the slits before a moving bar forces them back down into the grinding area where they continue until their size is sufficiently reduced to pass through the slits. Particle size is governed by air flow rate and the rotational speed of the slitted cylinder. Higher air flow rates and slower cylinder RPM lead to larger particle size in the finished powder. The refined powder collected from this mill has sufficiently small particles that no further grinding is needed when mixed with chocolate liquor that has also been ground to the proper size. However, since the sugar and milk particles have been ground in the absence of cocoa butter, this method generally requires a slightly higher fat content in the finished mixture to ensure adequate coating to meet the desired viscosity specification.

The proper particle size is necessary to impart a smooth texture to the chocolate, without creating excess fines that negatively affect chocolate viscosity. Particles greater than about 20 μm are detectable by the human palate, so refining should reduce particle size below this point if a smooth textured chocolate is desired. The particle size is governed by the intended characteristics and applications of the chocolate product. Coarser chocolate will need less of the costly cocoa butter to maintain a specific viscosity and less processing time is required. This will equate to a less expensive finished product and may be perfectly acceptable in certain applications such as a chip in a crunchy cookie.

However, grinding too finely is also not desired since extremely small particles give chocolate with a "greasy" character (too much cocoa butter is needed to coat these fines). Also, particles less than about 10 μm should be kept to a minimum during refining because of their dramatic effect on liquid viscosity. More fines lead to higher liquid chocolate viscosity, which then requires higher cocoa butter content to reduce viscosity to desirable specifications. Further details about the particle size distribution and the rheological properties of chocolate can be found in Section 15.5.3.

15.4.9 Conching

The traditional longitudinal conche, developed by Lindt in 1878, used a granite roller to continually mix and shear the liquefied chocolate. Continuously rolling the chocolate between the heavy granite roller and the longitudinal chamber led to improved flavor and enhanced smoothness of the chocolate. The conching process performs several complex functions that ultimately lead to a chocolate with improved flavor that can be easily differentiated from unconched chocolate. While conching in the early twentieth century may have lasted up to 3 days to ensure proper flavor development, new equipment design and controls can easily reduce this to a 4–24 h time frame. Some of the more important functions of the conch include reducing water content, smoothing out flavors, removal of volatiles such as organic acids, breaking agglomerated particles, and controlling finished chocolate flow properties.

The conch is essentially a high energy shearing device that continually works and turns the chocolate mass. In a conch, both shear mixing and elongational mixing occur. As the mixing device turns the chocolate mass, it is both forced between two surfaces (shear mixing) and forced to spread along a conche surface (elongational mixing). Shear forces depend on the gap between the mixing element and the wall of the conche, with smaller gap and higher mixer speed giving higher shear forces. However, smaller gaps mean that less chocolate mass is being sheared at any one time and thus, conches are designed to optimize the mass being sheared compared to the total mass in the conche. Figure 15.6 shows the complex shearing pattern in a common conche.

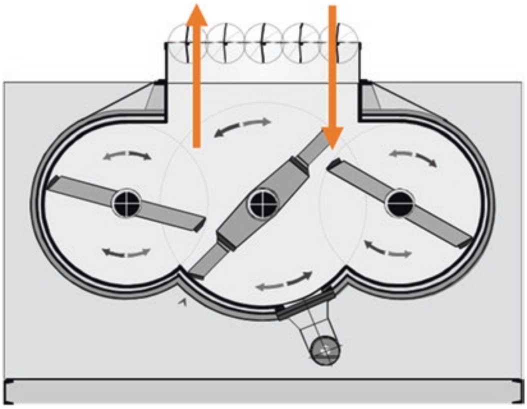

Figure 15.6 Cross-section of conche showing shearing action. (Courtesy of Bühler)

Typically, there are three stages of conching: dry, pasty and liquid. In the first stage, immediately as the powder from the refiner is introduced to the conche, the chocolate mass is dry and crumbly. In this stage of mixing, with relatively low cocoa butter content (about 22–25%), the particle surfaces are relatively well exposed to the atmosphere during shearing and here is where the majority of water loss occurs. Water content drops by about half, from about 1.5% in the refiner powder to less than 0.75%, in the first several hours of conching, although air ventilation, temperature, and humidity will also affect moisture loss. More gradual water loss occurs over the rest of the conche cycle. Along with moisture loss, volatile components, particularly acetic acid, are also released at this stage.

As the shearing forces work the chocolate powder from the refiner, its temperature increases and it gradually becomes more liquid, first going through a pasty stage. Liquification occurs, in part, due to the decrease in water content and, in part, due to the coating of small particles with fat. The rising temperature due to frictional forces also causes reduced viscosity. Often the RPM of the mixer is increased in this stage of the conche cycle to ensure adequate shearing. These shearing forces are critical to make sure any aggregated particles remaining from the refiner operation are fully broken down. Temperature and time are important parameters in conching and greatly affect flavor develop-

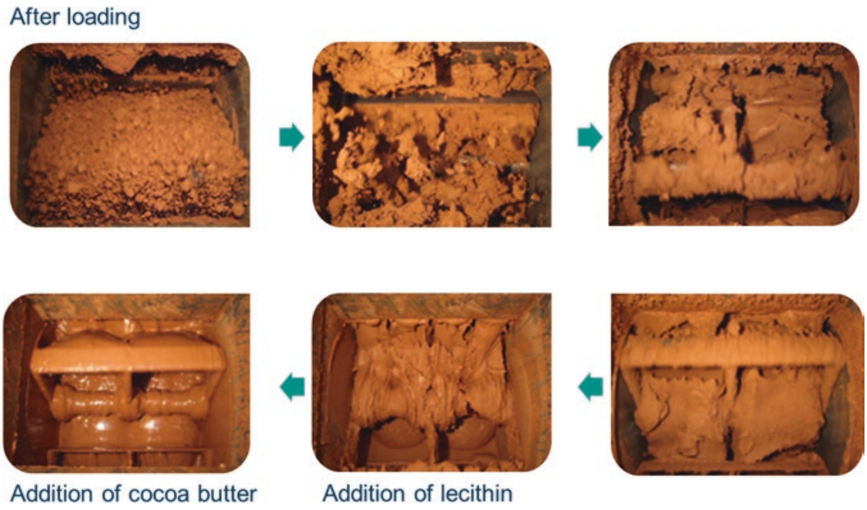

Figure 15.7 Changes in cocoa mass consistency during different stages of conching. (Courtesy of Bühler)

ment. Manufacturers use these to achieve the desired final flavor character. Conching temperatures can range from 60 °C (140 °F) to about 85 °C (185 °F).

The final stage of conching is the liquid (or wet) stage, where cocoa butter and emulsifier (lecithin and/or PGPR) and possibly flavorings are added. Here, the primary goal is to reach the finished product specifications for the chocolate. Final viscosity and fat standardization may be done at the conche or at a standardization tank further downstream. The changes in chocolate consistency at each stage in the conching process are shown in Figure 15.7.

Modern conching practice seeks to optimize each of the functions performed to influence chocolate smoothness, flavor and viscosity. Not surprisingly, because of the complexity of effects taking place in conching, numerous types of equipment have evolved over the years to accomplish these tasks. Conches may be batch or continuous. Batch conches are filled and go through each of the conching steps sequentially. These units are designed to employ both shear and longitudinal mixing to enhance moisture and volatiles loss. Continuous conches come in many different varieties, from a simple series of batch tanks operating at different conditions for each step of the process to carefully controlled continuous conches designed to efficiently control each function of the conche.

After conching, chocolate is stored untempered in heated jacketed tanks before being shipped in liquid tankers to customers or being pumped to a tempering unit for further operations. Liquid chocolate should be stored in tanks with slow or intermittent agitation to prevent oil separation with minimal incorporation of environmental odors and flavors. Storage temperatures can range from approximately 40 °C (104 °F) for white chocolate to 50 °C (122 °F) for milk and dark chocolates. Higher storage temperatures can cause white chocolates to become caramelized with a thick viscosity.

15.5 Tempering

In order for chocolate to solidify properly, it must be tempered to ensure that the cocoa butter crystallizes into the proper polymorph, the β V form (see Chapter 4 for more discussion of lipid polymorphs). It has been estimated that tempered chocolate contains from 1% to 3% of the cocoa butter in the form of small seed crystals in the β V polymorph, although the actual seed content required for good temper is substantially less (Kinta and Hartel 2010). Upon cooling, these seeds promote rapid solidification of the remaining liquid cocoa butter into the β V polymorph. Well-tempered chocolate contains numerous very small crystals in the β V polymorph that form a tight crystalline matrix. The exact size of fat crystals in solidified chocolate is unknown because it has proven impossible to distinguish individual crystals with any observation (e.g., microscopy) technique. Furthermore, the cocoa butter crystals likely interact in some form of network, which further exacerbates the problems of identifying individual cocoa butter crystals in solidified chocolate.

Well-tempered chocolate exhibits numerous desirable properties. Specifically, well-tempered chocolate solidifies quickly, contracts easily from a mold, exhibits high degree of snap and hardness at room temperature, has a shiny, glossy surface, and is resistant to bloom during storage.

Well-tempered chocolate solidifies quickly and this can be used to help determine if the degree of temper is acceptable. For example, an enrobed center in a cooling tunnel will set up in about 4–6 min with well-tempered chocolate while untempered or severely undertempered chocolate with the same set of conditions requires approximately 10–12 min. It should also be noted that the well-tempered chocolate will feel firm to the touch while the untempered chocolate will feel greasy and will readily melt in your hand. The rapid solidification of well-tempered chocolate is due to the rapid crystallization of the cocoa butter. In contrast, untempered, or even undertempered, chocolate takes a relatively long time to set up because the cocoa butter must first nucleate and without agitation, nucleation is a very slow process. Furthermore, undesirable β' crystals nucleate first and then slowly transform to more stable β V polymorph, causing numerous problems in the process.

Well-tempered chocolate releases easily from a mold because the cocoa butter contracts as it crystallizes since the crystalline matrix is significantly more dense than the corresponding liquid matrix. Seeded cocoa butter exhibits about 8% volume or 2% linear contraction when cooled to temperatures of 10–15 °C (50–59 °F) (Minifie 1989). This change in volume upon cocoa butter solidification results in a linear contraction on the order of about 0.8% in dark chocolate, depending on the nature of the fat phase. Milk chocolate, because of the moderating effect of milk fat on cocoa butter crystallization, contracts to a lesser extent. If chocolate is not well-tempered (or untempered), it crystallizes into the β′ polymorph, which does not contract to the same extent due to the relative disorder, and thus lower density, of the TAG molecules in the crystal lattice (see Chapter 4).

The hardness of well-tempered chocolate at room temperature imparts a desirable snap when a piece of chocolate is broken. The snap of chocolate can be affected by the degree and type of temper, amount and origin of the cocoa butter, and finally, the formulation of the chocolate that might include other fats. The tight cocoa butter crystal network provides this snap as well as the degree of hardness at room temperature.

Well-tempered chocolate exhibits a desirable shiny or glossy appearance (Afoakwa et al. 2008). This has been attributed to the presence of very small (micron size or less) fat crystals, some of which form a smooth layer at the surface of the chocolate (although this depends slightly on whether the air side or mold side of molded chocolate is studied). Chocolate surface roughness has been studied with either scanning laser microscopy (Briones et al. 2006) or atomic force microscopy (Rousseau and Sonwai 2008; Nightingale et al. 2011). Using atomic force microscopy, the surface roughness of fresh chocolate (given as the root mean square (RMS) roughness) is on the order of 0.12 μm, suggesting that the small cocoa butter crystals lie closely next to each other and other chocolate particulates (cocoa solids, sugar crystals, milk particles) do not extend out of the surface.

That tight crystalline cocoa butter matrix in well-tempered chocolate also provides a degree of stability against bloom formation. Since liquid oil migration is a necessary step for bloom to occur (Jin and Hartel 2015), a tightly packed network of cocoa butter crystals and other particulates provides the most resistance (an increasingly tortuous path) against liquid oil migration.

15.5.1 Tempering Methods

There are numerous ways to temper chocolate, with those methods being loosely categorized as to whether the molten chocolate is seeded in some way or whether the cocoa butter is forced to crystallize into the desired form. Any of the accepted tempering methods can work adequately as long as the end result in the tempered chocolate is a sufficient population of small seed crystals in the appropriate polymorphic form to promote proper solidification of the rest of the cocoa butter. However, since the fat phase (cocoa butter and milk fat) in each chocolate is slightly different, the conditions needed for optimal tempering vary slightly from chocolate to chocolate and generally need to be determined empirically.

Various seeding methods have been developed for tempering chocolate. One of the simplest methods of seeding chocolate to temper involves adding a quantity of well-tempered chocolate to the melted mass. The first step is melting a portion (about 90–95%) of the chocolate to at least 42–45 °C (107–113 °F) to erase any crystalline memory of the cocoa butter. The chocolate is then cooled to a temperature above the melting point of the cocoa butter – approximately 33–34 °C (91.4–93.2 °F). The remaining well-tempered solid piece of chocolate is added to the agitated untempered chocolate and is further cooled to a range of 29–31 °C (85–88 °F) depending on the formulation of the chocolate. When this temperature is reached, the chocolate is tested for temper. If found to be in temper, the remaining solid chocolate is removed to prevent overtempering. This type of seed tempering may be done by hand or in controlled-temperature tempering machines.

Chocolate may also be tempered by mixing in seed crystals of the desired polymorph. In this relatively simple process, a slurry containing seed crystals is mixed in an in-line mixer with chocolate at the temperature of about 32–34 °C (90–93 °F). At this temperature, cocoa butter is unlikely to crystallize (the kinetics of crystallization are very slow at this temperature), yet seed crystals of β V or β VI polymorph will remain intact. Some consider the crystal structure of the β VI polymorph to be best suited for seeding since it promotes rapid crystallization of the rest of the cocoa butter into the stable β V polymorph (Windhab 2009). Adequate agitation is needed to completely disperse the seed crystals into the chocolate mass. Seed levels between 0.2% and 2% of the chocolate mass are typically needed to ensure complete solidification of the chocolate during cooling. The time between seed addition and cooling is important to ensure that the seed crystals grow sufficiently to promote proper solidification but do not grow excessively while being held at warm temperatures.

A tempering method called the mush method is occasionally used in small chocolate processing facilities and culinary kitchens. It involves crystallizing a portion of melted chocolate by working it on a marble slab or a stainless steel cold table. A portion (between one-third and two-third) of the melted chocolate is poured onto a cold marble slab and worked continuously to about 27 °C (80.6 °F) and has become highly grained. This is observed as a dulling of the chocolate and a thickening of the viscosity. This crystallized chocolate is then mixed back into the remaining melted chocolate to reduce the temperature of the molten mass. The process may be continued until the resulting crystallized chocolate has reached the appropriate temperature 31–32 °C (88–90 °F). The chocolate is then tempered and ready for use.

In most manufacturing plants, tempering is done by mechanically inducing cocoa butter crystals. Chocolate is tempered continuously by passing it through scraped surface heat exchangers that expose the melted chocolate to a controlled thermal profile and intense agitation to induce crystallization (Figure 15.8). Time, temperature and agitation all contribute to the tempering process. These heat exchangers generally have three temperature zones. First, the chocolate must be fully melted to erase any cocoa butter crystal memory before being cooled to a temperature where nucleation of unstable polymorphs (primarily β′) is induced. This temperature depends slightly on the fat phase in the chocolate. Dark chocolates may be cooled to 27–28 °C (81–83 °F) whereas milk chocolate is cooled to a

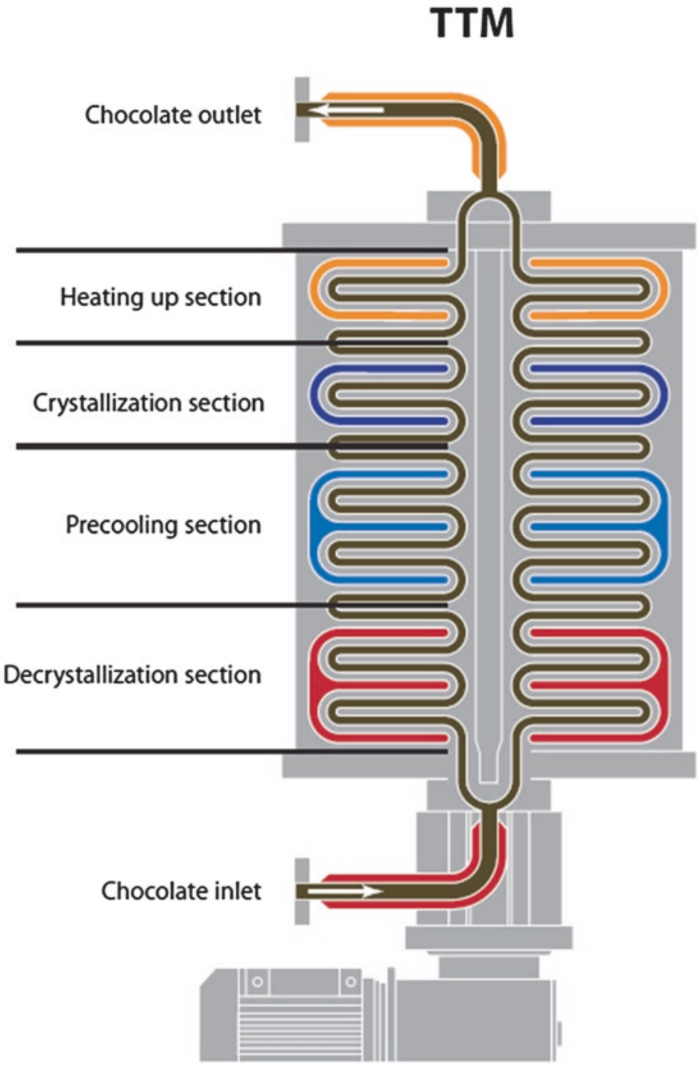

Figure 15.8 Continuous tempering unit (Courtesy of MF Hamburg)

slightly lower temperature, 26–27 °C (79–81 °F), to offset the inhibition of crystallization exerted by milk fat on cocoa butter. The final stage of the tempering heat exchanger raises the temperature of the chocolate to a point above the melting point of the unstable polymorphs but below the melting point of the stable β V polymorph. This causes melting of the unstable forms and transformation to the stable form. Temperatures on the order of 30–32 °C (86–90 °F) are common, but again, the optimal temperature depends somewhat on the nature of the fat phase in the chocolate. Figure 15.9 depicts the tempering process along with the state of cocoa butter at each stage.

15.5.2 Tempermeters

Determining the degree of temper in a chocolate is accomplished in a tempermeter. This is simply a cooling device that controls the rate of cooling while monitoring the temperature of the chocolate as it cools. A tempermeter is a type of calorimeter that, through measurement of temperature during cooling, documents the flow of heat during crystallization. Crystallization is an exothermic process (heat of crystallization), releasing heat as the molecules have less energy in the crystalline phase than in the liquid phase. Based on the nature of the cooling curve measured in the tempermeter,

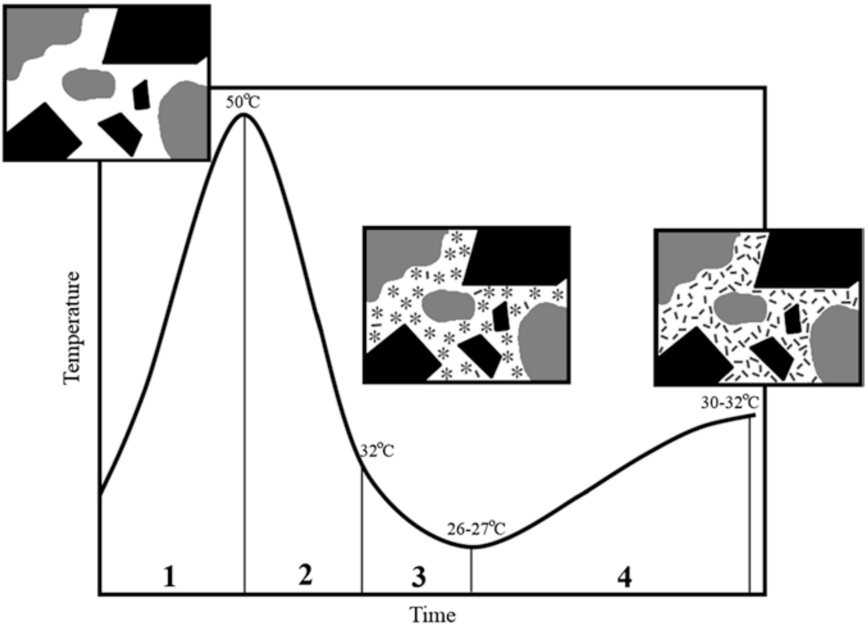

Figure 15.9 Schematic depiction of chocolate tempering with approximate state of cocoa butter. *Stars* represent unstable polymorphic forms while *bars* represent stable polymorphs

molten chocolate can be classified as untempered (no seeds), undertempered (too few seeds), well tempered (appropriate seeds) and overtempered (too many or too large seeds). These states are depicted schematically in Figure 15.10.

Tempermeters are designed so that a well-tempered chocolate exhibits a plateau in the cooling curve, as shown in Figure 15.11b. In this case, there is a period during cooling in the tempermeter when the heat of crystallization being released during solidification exactly offsets the decrease in temperature during cooling. That is, as the molten, but tempered, chocolate is cooled in the tempermeter, there are three stages of solidification. In the first stage, after the tempered chocolate is placed in the cooling tunnel, the change in sensible heat (temperature) of the chocolate occurs more rapidly than growth of the cocoa butter seeds in the tempered chocolate. Thus, temperature decreases in this stage. At lower temperatures, crystallization becomes rapid and the latent heat released directly offsets the cooling effect, leading to a plateau in temperature. Once crystallization is mostly completed, the cooling effect outweighs latent heat generation again and the chocolate continues to cool as a solidified mass (although a small amount of residual crystallization is still taking place).

If chocolate has an insufficient number of seeds (untempered or undertempered), the cooling profile in the tempermeter looks different (see Figure 15.11c). In this case, the first stage of cooling occurs as before, but at some temperature below the melting point of cocoa butter, the fat nucleates into unstable (mostly β′) polymorphic forms. Between nucleation of unstable polymorphs and growth of what seeds were present (in undertempered chocolate), there is a relatively large release of latent heat such that the temperature of the chocolate begins to increase, despite the fact that it is in a cooling bath. That is, the heat of crystallization is sufficiently large to reverse the cooling effect in the tempermeter. In this case, the tempermeter cooling curve exhibits a peak in the temperature profile, recorded as a positive slope by the tempermeter. Untempered and undertempered chocolates do not exhibit the desirable attributes of well-tempered chocolate. Specifically, undertempered chocolate takes longer to set up than tempered chocolate and does

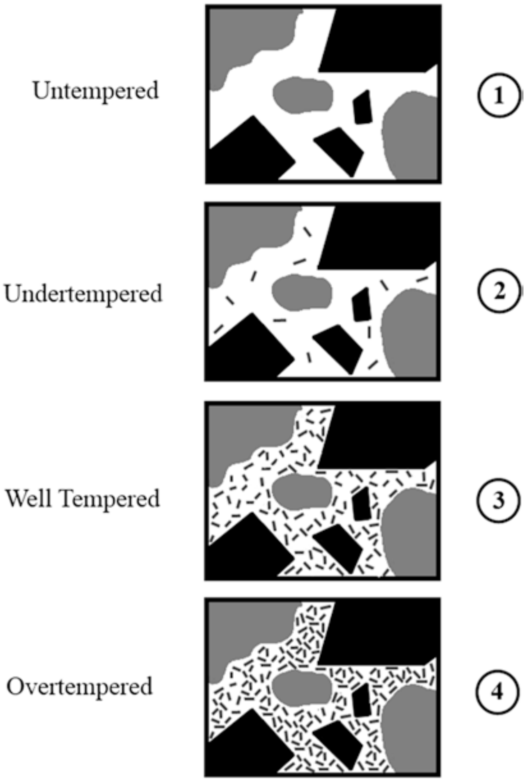

Figure 15.10 Schematic drawing depicting (*1*) untempered, (*2*) undertempered, (*3*) well-tempered, and (*4*) overtempered chocolate

not become as solid; thus, it has poor snap, does not contract very well from molds, and blooms readily (usually within 1–2 months). Untempered chocolate has all of the poor attributes of undertempered chocolate only to a greater degree and bloom is generally seen almost immediately. Interestingly, some chocolates bloom more rapidly when untempered than others, with some chocolates taking several days to show the onset of spots (Hartel unpublished results). Besides the whitish surface appearance of bloom, a coarse crumbly texture is also seen.

In contrast to undertempered chocolate, overtempered chocolate contains either too many or too large cocoa butter seeds. When cooled in a tempermeter, there is insufficient crystallization so that the latent heat generation never offsets the cooling effect and the tempermeter curve shows a continuous decrease in temperature (Figure 15.11a). Depending on the level of overtempering, a slight delay in the cooling curve may be seen, although severely overtempered chocolate exhibits a simple logarithmic cooling profile similar to the cooling curve of a solid mass that undergoes no phase change. Overtempered chocolate gives a negative slope in the tempermeter, with higher negative slope indicative of greater degree of overtemper. Overtempered chocolate is significantly more viscous than tempered chocolate, meaning it does not flow in enrobers or into molds as easily, potentially causing appearance defects such as air bubbles. Also, overtempered chocolate does not form the cocoa butter crystal structure necessary for a glossy surface appearance, with the surface of overtempered chocolate appearing dull instead.

In the tempermeter, the slope near the plateau of heat production by cocoa butter crystals is often used to represent the degree of temper. Some tempermeter manufacturers specify degree of temper through units related to the slope of the heat trace near the plateau point. If the slope is 0, meaning the plateau is perfectly flat, the chocolate is well tempered. A positive slope indicates undertempering and a negative slope indicates overtempering (Figure 15.11).

15.6 Forming

Once melted chocolate has been tempered, it is ready for application and use. Numerous methods of forming chocolate have been developed over the years although these may be broadly grouped as depositing or molding, enrobing, and panning. Viscosity parameters (yield stress and plastic viscosity) should be controlled appropriately for each different forming method. See Section 15.8.3 for more details about rheology requirements for each method of forming.

15.6.1 Depositing/Molding

Probably one of the first methods developed for using chocolate was solid molding. This is the simple process of depositing the tempered mass into a mold of the desired shape and allowing it to cool and solidify. The entire process of filling the

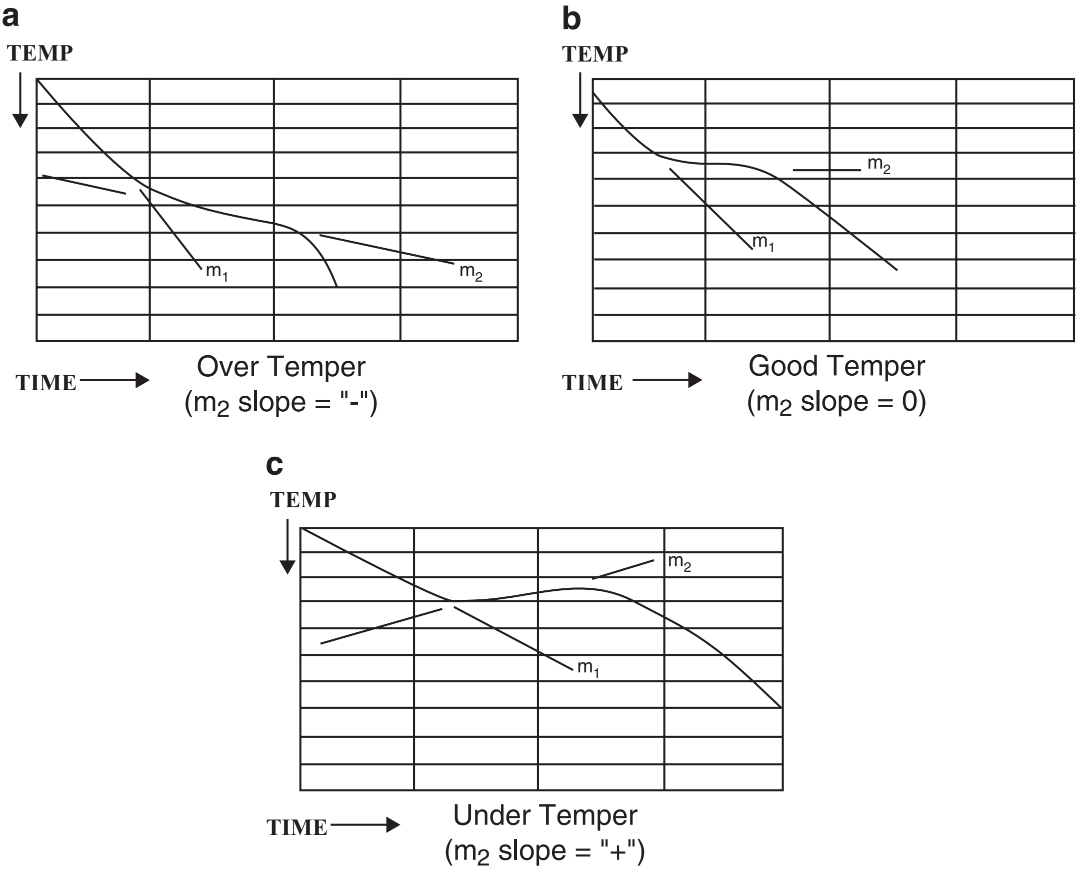

Figure 15.11 Typical temper meter curves for (**a**) overtempered, (**b**) tempered, and (**c**) undertempered chocolate (Courtesy of Tricor Systems)

molds, cooling to solidify the chocolate, and demolding the pieces can be done by hand, but now is more commonly done on continuous molding machines. Cleaned and temperature conditioned molds are fed into the depositing zone of the molding unit, where tempered chocolate is filled into the depressions in the mold. The molds are vibrated with the proper intensity and frequency to allow the fluid chocolate to fill the entire mold and release any air bubbles before being conveyed through a cooling tunnel to solidify the chocolate. Upon exiting from the cooling tunnel, the molds are inverted, twisted and the chocolate pieces removed. The molds are circulated back to the start for re-use while the chocolate pieces continue to packaging and shipping. Usually the molds are separate forms moving on the conveyor, but some larger units may have the molds fixed into place on a conveyor that makes a continuous circuit of the depositing, cooling and demolding cycle.

The majority of molds used in industrial processes are polycarbonate. They may be simple in shape (i.e., blocks or bars) or may take any unique shape desired by the chocolate maker (i.e., Santa, Easter Bunny, or any other specialty item). Molds may have few details, may contain an inscription of the company name, or may contain fine details and shapes (e.g., buttons on Santa's coat). Having details in the molds help the release process and reduces the tendency for ‘pull’ or ‘kiss’ marks. Rheologically, the chocolate used for molds with fine details must have low viscosity and low yield stress (see Section 15.5.3) so that it can flow easily to fill each nook and cranny of the mold. The low viscosity also helps prevent air bubble entrapment. Molds must be at the right temperature when the chocolate is deposited. If the molds are too warm, the chocolate may break temper in the surface region if temperatures are sufficiently high to melt the seed crystals. Uncontrolled crystallization will then occur at the surface, leading to unsightly appearance of the chocolate as well problems with demolding. If the mold is too cold, on the other hand, several problems may arise. First, very cold temperatures can cause undesired nucleation of unstable cocoa butter crystals, which then gradually transform to more stable polymorphs. This causes problems with bloom formation and lack of gloss at the surface. It also decreases the volume contraction of the piece, causing problems with demolding. Second, cold mold temperatures can impair the ability of the chocolate to flow, with potential problems of filling fine details in the mold shape. Finally, cold molds may have condensate, which will lead to demolding problems and sugar bloom. Typically, mold temperatures should be approximately 1 °C (2 °F) less than the chocolate being deposited.

Depositors for chocolate come in various sizes and types, but are typically either piston or rotary depositors. For piston depositors, when the deposit stroke is finished, the pistons are at their lowest point, the slide bar valve closes (no further depositing), an inlet valve in the slide bar is opened and the pistons rise, sucking liquid tempered chocolate in from the hopper. Once the piston is filled, the slide bar shifts to open the channel to the nozzle plate, the pistons descend and the chocolate is pushed out through the nozzles.

Rotary depositors are similar to a rotary positive displacement pump, with each discrete packet of chocolate released through the nozzle to fill into the mold cavity. A hopper filled with tempered chocolate feeds the depositor mechanism, which is sequenced to deliver the desired amount of chocolate into each cavity as the mold passes underneath on a conveyor. To cleanly break the chocolate tail after each deposit shot, either the nozzle or the mold is pulled away at the end of the stroke. To also assist with the elimination of chocolate tails, ‘suck back’ is employed. This is the reverse action of the piston or valve after depositing to cause a reverse flow of the chocolate tail.

Molded chocolates may also be filled with fluid or semi-fluid centers in shell molding. There are numerous ways to accomplish shell molding, from hand-made artisan-style filled chocolate to high capacity continuous depositing lines, although they all generally follow the same protocol. For the traditional three-step molding process, a dose of tempered chocolate is deposited into the mold, either by hand or by depositor, sufficient to completely fill each depression. To ensure adequate coverage of the entire depression and release any air bubbles, the mold is vibrated or shaken. The mold is then inverted and shaken to release liquid chocolate, leaving a shell filling in each depression of the mold. The surface of the mold, while inverted, is scraped to remove any residual chocolate. Shell wall thickness must be uniform to prevent cracking. The shell is allowed to cool and solidify before being filled with whatever filling is desired. Typical fillings include ganache, caramel, meltaways, creams or any other semi-fluid center material. It is imperative that just the right amount of filling is added. Too much filling and the chocolate bottom will not seal correctly, whereas too little filling leads to an imbalanced piece with too much chocolate.

After the shells are filled, the top of the mold and the upper rim of the chocolate shell are briefly warmed before a bottom layer of tempered chocolate is applied. Warming allows the two chocolate surfaces to bond and minimize air bubble formation. The molds are then scraped clean, shaken to release air bubbles and allowed to cool. Typically, the bottom chocolate must have relatively low viscosity in order to quickly fill and seal the piece. If done correctly, the bottom layer of chocolate fuses with the shell chocolate, giving a single intact piece with the appropriate amount of filling material. Once the entire piece has been cooled and sufficiently set, the mold is inverted, twisted and struck sharply (or torqued) to release the filled chocolates. The molds are warmed and re-used while the chocolates continue on for sorting and packaging. Molds usually do not need cleaning if tempered chocolate and proper cooling and rewarming procedures are used. If an accumulation of chocolate occurs, the molds are gently cleaned and dried with no residual water marks. Harsh cleaning methods can damage the smooth interior surface of the mold and result in poor demolding.

Tempered chocolate can also be deposited directly onto a belt to form drops, chips or wafers. Here, a measured quantity of chocolate is deposited directly onto a conveyor belt, which then takes the chocolate directly into a cooling tunnel to set up. At the end of the cooling tunnel, solidified chocolate drops fall off the conveyor, ready for packaging for either retail or wholesale use. Many chocolate suppliers produce chocolate in the form of wafers for sale to manufacturing companies. The wafer shape is easy to melt and simple to use. To make drops or chips requires careful control of rheological properties of the fluid chocolate. Specifically, the ability of fluid chocolate to resist flow after being deposited on a belt is dependent on the yield stress (see Section 15.8). To make a drop or chip requires a chocolate formulated to give a high yield stress, one that resists flowing into a thin puddle before it can be solidified. After a dollop of chocolate is deposited on the conveyor, the only force acting on the fluid chocolate is the force of gravity. Thus, for a chocolate to maintain its height after depositing, the yield stress should exceed the force of gravity. Product deformation can also be reduced by minimizing extraneous belt movement.

Recently, single-shot depositors have become popular for producing a variety of shapes and forms of filled chocolates. Single-shot depositing, so-called because both chocolate and filling are released through a complex nozzle in one single shot, allows quick and easy manufacture of filled chocolates. For efficient operation, however, careful control of both formulations (chocolate and filling) and process operations are required. Use of single-shot depositing is also limited to those fillings that are sufficiently fluid to be pumped and deposited. The depositor nozzle for single-shot technology contains two separate depositing elements, both timed to work carefully together. The outer (or annular) nozzle deposits chocolate while the interior nozzle deposits the filling. Single-shot depositing may be used to make filled bars, filled drops or wafers (or kisses), filled eggs or center-filled chocolates (similar to those made in shell molding). Timing of the single-shot depositor is critical to getting the correct level of fill and a complete seal of the chocolate. As shown in Figure 15.12, flow of

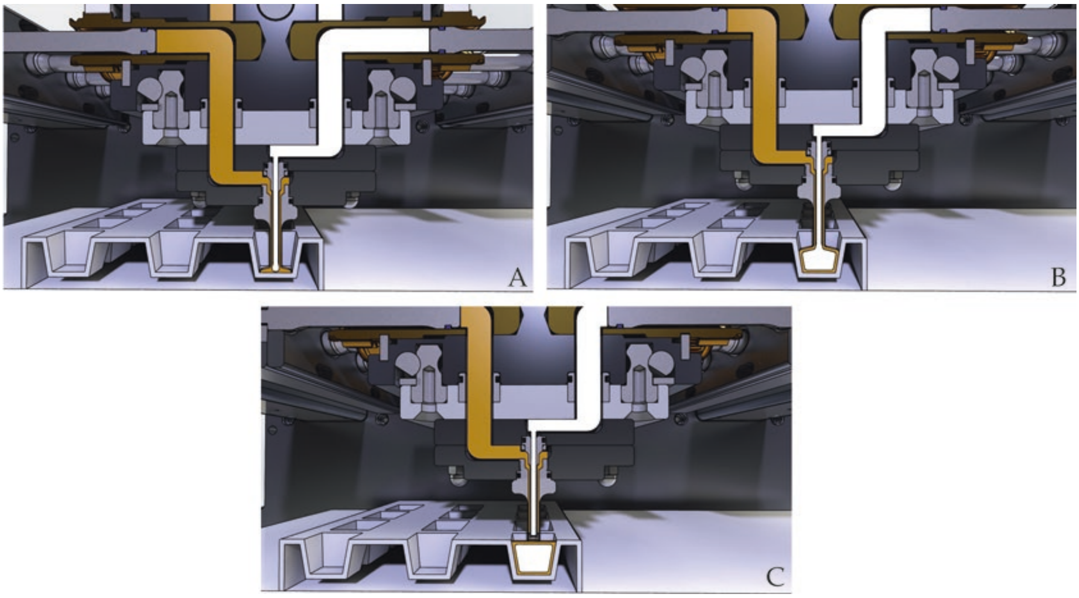

Figure 15.12 Schematic operation of single-shot depositor. (**a**) Initiating flow, chocolate first; (**b**) Filling; (**c**) closing with filling shut prior to chocolate (Courtesy of Hacos van Meulenbeke)

chocolate through the outer nozzle starts the depositing sequence. Chocolate flows to fill the bottom of the mold cavity after which the center nozzle opens (while chocolate is still flowing) to create a filled tube of chocolate. The chocolate and filling flow together to take the form of the mold. When sufficient material has been deposited, the filling nozzle stops while chocolate continues to flow. At the point when the chocolate layer meets to complete the shell, the chocolate flow is stopped and the nozzle (or mold) pulled away to prevent tailing. If depositing is sequenced properly, the correct amount of filling is co-deposited into the chocolate, giving a single piece of extremely uniform size, shape and weight. Typically, filling levels can vary from 40% to 55% of the piece weight, although some single-shot products, like filled chocolate eggs, may have much higher ratios of filling to chocolate. In order for single-shot depositing to work efficiently, the viscosity of filling and tempered chocolate viscosity (which is higher than viscosity of molten chocolate because of the added cocoa butter seed crystals) must be carefully matched, a requirement that limits the nature of the fillings that can be used. Careful control of filling formulation, chocolate temper and temperatures of both components is necessary to ensure proper viscosity control and efficient single-shot operation.

In each of the methods described so far, the chocolate has been deposited either into a mold or onto a belt. Depositing into a mold typically makes a chocolate with a flat top as the liquid chocolate flows to form a level surface. To make three-dimensional molded pieces, the chocolate must be deposited into a three-dimensional mold. One such mold is the book mold, aptly named because two sides of a flat mold hinged together on one side are closed like a book to form a three-dimensional piece. In book molding, tempered chocolate is first filled into both sides of the mold. For solid forms, the entire mold form is filled, whereas for hollow pieces, the excess chocolate is shaken out of the mold form in the same manner used for shell molding. Once the two sides have set, the chocolate at the intersection point (the flat surface for solid shapes and the lip for hollow shapes) is warmed and the mold is closed so the two sides overlap. In hollow forms, a chocolate lip may be applied in a separate step to ensure proper sealing of the two sides. Upon cooling, the two sides fuse together, forming a three-dimensional shape with an overlapped seam of fused chocolate.

Another method of making three-dimensional hollow chocolate shapes uses a book mold with a spinning device. In this case, the proper weight of tempered chocolate is filled into one side of the mold, the mold is clipped closed and attached to a special spinning machine designed to rotate the mold in two directions. The rotating arm on which the mold is clipped spins around in the vertical direction while also rotating in the perpendicular direction. The multi-directional spinning motion of this unit allows the fluid chocolate to create a shell of uniform thickness in the mold. The thickness of the shell is determined by the amount of chocolate initially loaded into the mold. Once the chocolate has completely solidified, the mold is removed from the spinner and opened to release the hollow shape within. The same process can be done by hand to make specialized pieces or larger pieces; for example, some hollow chocolate bunnies, for example, may be up to 1.2 m (4 ft) tall.

15.6.2 Enrobing

Coating a candy piece in chocolate can be accomplished by hand dipping or fork dipping, where the center is manually immersed in tempered chocolate and then placed on a tray for cooling and solidification. Although hand dipping gives a unique craft feel to chocolates, the process is slow and tedious. The automated process of coating a candy piece in chocolate is called enrobing. The process of enrobing involves passing a center through a curtain of tempered chocolate to create a thin chocolate shell on the top and sides of the piece. Since the enrober curtain only covers the top and sides of the piece, a separate bottoming device is needed to ensure complete coverage. The bottomer is typically a roller or plate that transfers tempered chocolate from underneath the wire belt to the bottom of the confection piece. The piece on the wire belt is conveyed through the bottomer chocolate, sometimes by use of a hold-down device to make sure very light weight centers get complete bottom coverage. A bottomer may be used either before or after the curtain. To obtain a thicker bottom, a pre-bottomer is placed before the enrober to coat the bottom of the piece with a thicker layer of chocolate or compound coating to ensure an adequate seal of soft centers. A cooling step may be required after the pre-bottomer to ensure complete solidification before entering the enrober. A typical enrobing process is shown in Figure 15.13. The coated center after leaving the enrober is then conveyed through a cooling tunnel to solidify the chocolate prior to packaging.

Enrobing systems come in different configurations depending on the sophistication of the machines and product requirements. All elements must be in good operating condition to produce uniformly coated pieces that are attractive to the final consumer. These will usually include a tempering unit, chocolate curtain, blower, bottoming roll, shaker, licking roll, detailing rod and a wire belt to convey centers through the enrober to the cooling tunnel. Most enrobers have a temperature-controlled cabinet to help maintain consistent temper during this operation.

As with all chocolate applications, it is a basic necessity to have well-tempered chocolate. In an enrober, tempering may be accomplished by seeding or with either an internal or an external tempering unit.

The smallest enrobing units typically contain a kettle or trough of tempered chocolate from which the curtain is formed. A pump or other riser element (e.g., a chain or wheel) carries the tempered chocolate to the hopper for forming the chocolate curtain and the unused chocolate falls back into the kettle for re-use. Proper chocolate temper in such units can be a challenge, with the chocolate often prone to overtempering, which may require periodic shut downs for re-tempering.

Alternatively, a built-in tempering unit (in-board) may be included in the enrober unit in order to ensure well-tempered chocolate is continually fed to the enrober curtain. In-board tempering units have a reservoir, or sump, to catch the unused chocolate, a heating unit (for detempering) to raise the temperature of the chocolate to about 45 °C (123 °F) to melt cocoa butter crystals and a small tempering unit operating in a continuous cycle. The product exiting the in-board tempering device is pumped up to the curtain trough where it falls uniformly in a curtain of well-tempered chocolate to coat the pieces passing through on a wire conveyor (Figure 15.13).

Figure 15.13 Chocolate enrober. (Courtesy of Sollich North America LLC)

Enrobers with an external tempering unit (outboard) maintain ideal chocolate temper by recirculating a portion (10–20%) of the chocolate mass through an external loop that contains a detempering heater, a sieve for screening out particulates from centers, and a surge tank that will feed the tempering unit. This tempered chocolate is remixed with chocolate already in the sump for pumping up to the curtain trough for enrobing.

Well-tempered chocolate is pumped to a trough from which the curtain of chocolate falls. The trough may contain an adjustable slot at the bottom to allow a controlled amount of liquid chocolate to fall through, with the width of the slot determining how much chocolate is allowed through. Alternatively, rotating rollers at the bottom of the trough are used to carefully control the amount of chocolate allowed to form into the curtain. To give thicker coatings, enrobers with multiple chocolate curtains in series may be used. For larger enrobers, multiple chocolate feed points into the curtain trough may be necessary to ensure consistent flow to the pieces that will be enrobed.

After the center passes through the chocolate curtain and bottomer roll, several subsequent operations may be necessary to ensure the desired coating characteristics are attained. To remove excess chocolate, the center first passes under an air blower and then onto a shaking device on the wire belt. Air velocity of the blower and amplitude and frequency of shaking can be adjusted to help obtain the desired percentage of chocolate. All of the excess chocolate that is removed by blowing or shaking is returned to the sump for re-use. Many enrobers have a licking roll to remove excess chocolate from the bottom of the centers before they exit the enrober. This helps prevent a wide bottom (foot) from forming when it is on the cooling tunnel belt. Virtually all enrobers have a detailing rod to help prevent 'tails' from forming on the exit side of the coated piece. Located just after the wire belt and before the cooling tunnel belt, the detailing rods must be properly adjusted to prevent 'tails' from forming, but also so that all of the coating bottom is not removed from the center. They typical rotate in reverse (countercurrent), but in certain cases such as with smaller pieces, they may rotate with the flow of the product to assist with transfer to the cooling tunnel belt. Decorating units may apply patterns on the top of the enrobed piece, either with the same chocolate as used in the enrober or a different color to provide contrast. These units can apply numerous different types of designs (zigzag, single loop, double loop, cross-hatch, etc.) to provide an attractive appearance to the enrobed piece. It should also be noted that coated pieces that have some type of design on them generally have more of a shiny appearance due to a greater reflective area on the piece.

The thickness of the chocolate coating on the center is governed by a number of parameters. First and foremost is the rheology of the chocolate, particularly the yield stress (see Section 15.5.3). Chocolate with a high yield stress results in a thicker chocolate coating whereas a low yield stress gives a thinner coating. Proper specification of the chocolate is required to match the intended application. Other parameters that affect the thickness of an enrobed chocolate layer include the speed at which the piece passes through the curtain, the temper of the chocolate, and the subsequent steps of blowing and shaking intended to remove excess chocolate from the center.

Once the piece has been enrobed, it passes through a cooling tunnel designed to quickly and efficiently solidify the chocolate (see Section 15.7). As the product exits the cooling tunnel, it is sorted and collected for packaging.

15.6.3 Cold Forming Shell Technology

Cold press forming technology, as seen in Figure 15.14, allows for rapid formation of a chocolate shell through the use of a cold plunger (Aasted 1997). The technology produces extremely uniform shells in a fraction of the time needed for typical shell molding methods. First, a specified amount of tempered chocolate is deposited into a mold. The amount of chocolate should be just slightly more than the amount required to form the desired shell – this is significantly less chocolate (about half) than needed in traditional shell molding technology. A cold plunger with

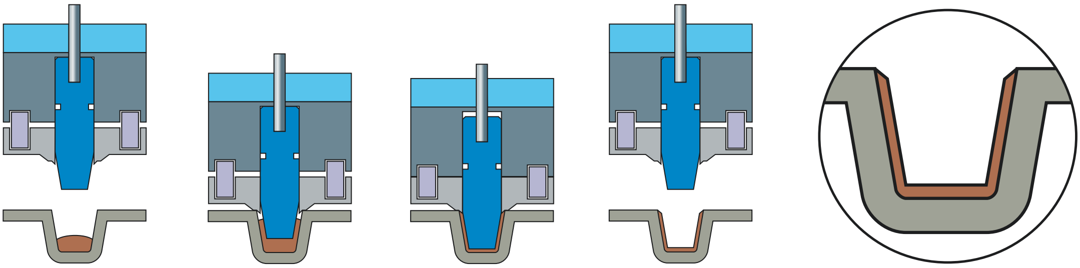

Figure 15.14 Schematic operation of cold press technology for making chocolate shells. From *left to right* – chocolate filled into mold, cold press comes down into chocolate, cold press compresses the chocolate into the mold, and then releases, leaving a uniform chocolate shell within the mold (Courtesy of Aasted ApS)

the same shape as the mold is forced into the tempered chocolate such that the chocolate is forced into a thin layer. The plunger needs to be extremely cold, on the order of −21 to −5 °C (−6 to 23 °F), to press the chocolate into shape. The plunger needs to remain intact in the mold for enough time to solidify the chocolate so it can be removed without sticking. Typically, this is 2–5 s, depending on plunger temperature. As expected, colder plunger temperatures require less time for solidification. Once the plunger is removed, the edges are scraped level and the centers filled as previously described for shell molding technology (see Section 15.6.1).

Cold press technology has several distinct advantages over other forms of shell molding. First, because of the specially designed plunger and mold set, the thickness of the chocolate shell is extremely uniform and can be precisely controlled. And, this high level of control can be accomplished using significantly less chocolate than normally used in shell molding. Furthermore, the strict viscosity requirements for molding chocolate are no longer necessary since cold press technology can accommodate a wider range of chocolate rheology. These advantages come at the cost of purchasing new plungers and molds for each new mold design. This can be expensive due to the close tolerances needed.

Remarkably, the extreme cold used in this technology does not cause undesired crystallization of the cocoa butter, primarily due to the rapid setting process. Because of the short exposure times, the cold-pressed chocolate shell does not have sufficient time to nucleate unstable forms; thus, only the seeds of well-tempered chocolate grow out in the cooling tunnel, in exactly the same way as for the normal shell molding process.

15.6.4 Extrusion Forming

Various attempts have been made to develop an extrusion process for forming of chocolate, and several have seen commercial application. Such cold extrusion processes, however, require a material with much higher viscosity than typically found in tempered chocolate. Thus, the chocolate must be cooled to promote more extensive crystallization without complete solidification to produce a semi-plastic state that can be worked in the extruder. Precise control of temperature and crystallinity is necessary to control viscosity and obtain satisfactory extruded products.

Various chocolate shapes have been extruded, although what can be done is limited somewhat by the nature of the chocolate itself. The most successful application of extruded chocolate seems to be interlaced chocolate nets or mesh that can be used as decoration on top of other confections or baked goods. However, ropes and sticks of chocolate have been extruded as well, sometimes exhibiting unique behavior and properties. For example, Mulji et al. (2003) show a rope of extruded chocolate that retained sufficient pliability for a period of time such that it could be folded into a knot. This pliability following extrusion was correlated to an anomalously high liquid fat content immediately after extrusion. Ovaici et al. (1998) documented two different types of instability seen in extruding chocolate at room temperature. One, called the stick-spurt instability, occurred at low flow rates and resulted in ropes of different diameters despite no change in processing conditions. The second instability, named the Ovaici necklace, was seen under a specific thermal history and led to extrusion of a thin rope with periodic “beads” of larger diameter that were reminiscent of a necklace shape.

15.6.5 Aeration

Aerated chocolate is a unique product, employing specialized equipment for production. Aerated chocolate gives a light, fast melt-in-your-mouth sensation, while adding volume to the piece through incorporation of small gas bubbles. This gives the bar a larger visual appeal for a given weight.

There are two main methods of manufacturing aerated chocolate. The traditional method involves tempering chocolate and depositing into a mold. The partially filled molds enter into a special cooling tunnel that is under vacuum. The chocolate expands under the negative pressure and maintains the aerated structure as it solidifies. The size of air bubbles in the final chocolate depends on numerous factors, including applied pressure and other ingredients including emulsifier, milk fat, and others (Haedelt et al. 2005).

The other method of producing aerated chocolate utilizes a gas (e.g., carbon dioxide or nitrogen) dissolved into the tempered chocolate under pressure. When the pressurized chocolate is released to atmospheric conditions, as the chocolate fills the mold, it causes the chocolate to expand and maintain its light density as the cocoa butter hardens around the air pockets.

15.6.6 Panning

Coating various pieces in chocolate is a common operation that allows production of a wide variety of candies. Fruits, nuts, seeds, malted milk balls, candy pieces, and cookie dough are examples of the types of centers that can be panned in chocolate (or compound coating). Chocolate panning is covered in more detail in Chapter 17.

15.7 Cooling Tunnels

Tempered chocolate after forming requires careful cooling to ensure that the cocoa butter seed crystals solidify the remaining cocoa butter in the proper crystal polymorphic form. If cooling is not done correctly, unstable crystals can still form, leaving a chocolate without the desired attributes. In a sense, cooling is the continuation of good tempering and should lead to chocolate with a glossy appearance, adequate contraction from a mold, and resistance to bloom formation. During cooling, the continuation of cocoa butter crystallization causes a subsequent release in latent heat, as seen in the temper meter curves (see Section 15.5.2). Typically, temperatures are controlled to provide the most efficient heat removal and solidify the chocolate in the shortest time possible while still retaining proper cocoa butter crystal types. Dwell times in a cooling tunnel depend somewhat on the size of the article, and may vary from 6 to 10 min for small enrobed pieces to over 2 h for large molded blocks.

A typical cooling tunnel with one example of potential air flow circulation is shown in Figure 15.15. In a cooling tunnel, the cooling system must remove both the sensible heat (lowering temperature) and the latent heat (heat of crystallization). Careful control of heat transfer is required to optimize cooling and minimize the time spent in the cooling tunnel. Heat transfer in a cooling tunnel primarily comes from a combination of conduction, from the bottom of the chocolate to the conveyor belt, and convection, heat transfer from the chocolate to the cool air circulating in the tunnel. In some cooling tunnels, radiation cooling from absorber plates may also occur.

The rate of heat transfer in a cooling tunnel is typically staged to account for the changes in chocolate during solidification, particularly the rate of crystallization. In the periods of the most rapid crystallization, and most rapid release of latent heat, the rate of heat transfer must be high.

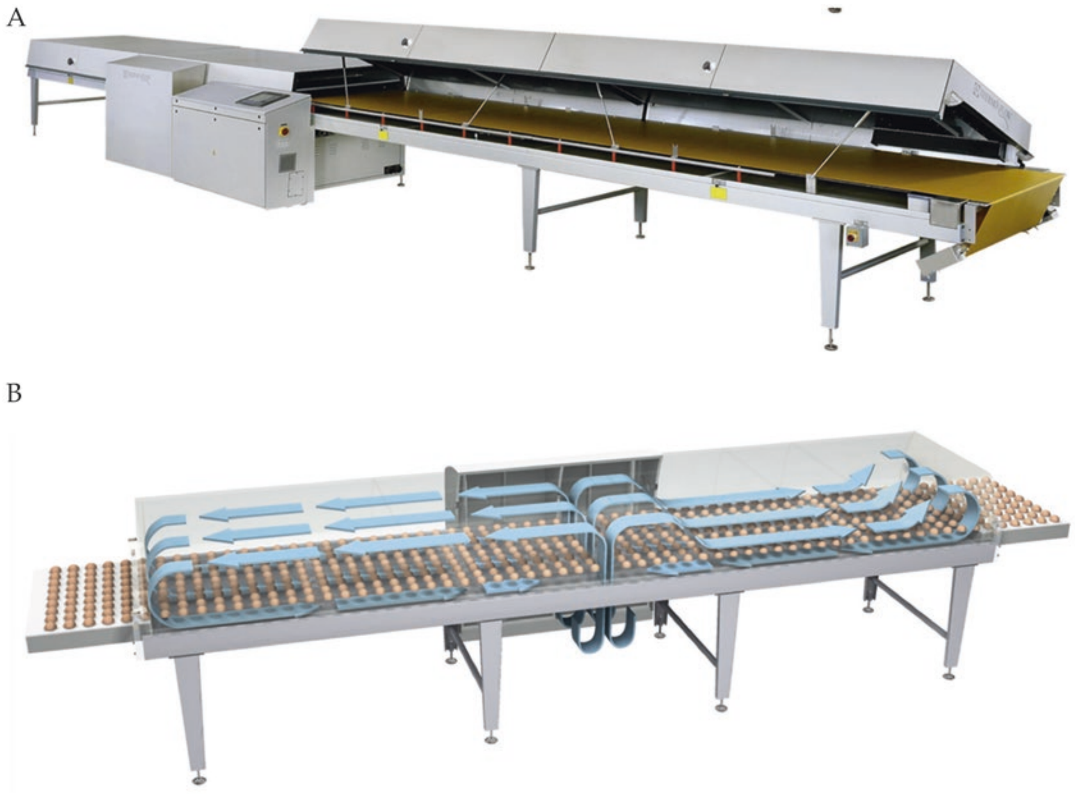

Figure 15.15 Chocolate cooling tunnel. (**a**) Half-opened; (**b**) Air flow (Courtesy of Sollich)

At other times in the solidification process, heat transfer rates may be significantly lower to prevent undesirable effects. Cooling tunnels designed for conduction and convection heat transfer can control rate of cooling in two ways, through control of temperature and air flow. Colder temperatures drive faster heat transfer whereas higher air flow increases heat transfer through an increase in the convective heat transfer coefficient.

Consider a block of tempered chocolate as it enters a cooling tunnel at depositing temperature of about 29–30 °C (84–86 °F). As the chocolate starts to cool, the cocoa butter seed crystals present in the tempered chocolate begin to grow, releasing heat. However, initially this process is relatively slow, only picking up in speed as temperature decreases a little further into the tunnel. Thus, the initial heat transfer requirements in the cooling tunnel are not as high as they will be later, when crystallization becomes much faster. If heat transfer is too fast in the early stages of the cooling tunnel, through either very cold temperatures or high air velocity, there is a possibility of unstable polymorph nucleation and poor heat transfer from the interior of the block. The result would be unacceptable solidification of the chocolate, leading to loss of gloss and, in the most extreme case, to rapid bloom formation. For this reason, the initial stages of a cooling tunnel have moderate temperatures, with air temperatures in the range of 15–17 °C (59–62 °F). Further, reduced air flow is used in the first section to ensure slower cooling.

Once the chocolate has cooled to a point where rapid solidification of the chocolate occurs, there is a significant release of latent heat as much of the cocoa butter crystallizes. If not removed quickly, this latent heat would slow down crystallization, potentially even causing an increase in temperature. If left unchecked, the heat released may even cause melting of seed crystals in the tempered chocolate not yet solidified in the interior of the chocolate piece. Breaking seed in this way can lead to a form of internal bloom sometimes seen in large blocks of chocolate. In this stage of the cooling tunnel, rapid heat transfer is desired so temperatures are lowered significantly and air flow is high. Temperatures may be in the range of 7–13 °C (45–55 °F), although actual temperatures may vary slightly with the type of chocolate, tunnel design, air velocity, and enrobed vs. molded vs. deposited format. Typically, milk chocolates require slightly lower temperatures than dark chocolates to offset the inhibitory effects of milk fat on cocoa butter crystallization.

Once the majority of cocoa butter has completed crystallization, the nearly solidified chocolate no longer needs to be cooled. In fact, the tunnel air generally needs to be warmed somewhat to ensure that the chocolate's temperature is above the dew point of the ambient air as it exits the tunnel. If not, condensation of moisture from the air occurs on the cold chocolate surface, causing sugar bloom (see Section 15.9.1). The chocolate is warmed to about 15.5 °C (60 °F) to prevent moisture condensation as the chocolate exits the tunnel. Temperature and humidity control in the plant are needed to ensure proper operation of the cooling tunnel and to prevent moisture condensation problems.

To summarize, based on the different heat transfer requirements at different stages of solidification, most cooling tunnels have three zones where temperature and air flow are controlled. The first stage gives moderate cooling (moderate temperatures and minimal air flow) in order to avoid undesirable nucleation of cocoa butter. The second stage is where the bulk of the heat of crystallization is removed so lower temperature and higher air flow are typically used. Franke (1998) modeled heat transfer and crystallization rate in the first two stages of a cooling tunnel to optimize operating conditions based on different chocolate products. The final stage of the cooling tunnel uses warmer air to raise the chocolate temperature above the dew point to prevent problems as the product exits the tunnel into ambient air.

Some cooling tunnels incorporate radiation cooling through a cold black plate above the chocolate product. Radiation heat transfer occurs from the warmer chocolate to the black body absorber. However, the amount of heat transfer through radiation is generally considered to be a relatively small percentage of heat transfer through conduction and convection.

15.8 Chocolate Characteristics

The characteristics of chocolate that make it such a popular product and ingredient are numerous and varied. From the delectable flavor to the characteristic snap to the melt-in-the-mouth sensation, the desirable characteristics of chocolate are what has made chocolate one of the most sought after treats for generations. Careful control of these properties is required to create high quality chocolate.

15.8.1 Flavor

To paraphrase Ed Seguine, a noted chocolate scientist and educator,

> *Chocolate is an extremely complex material. If you mixed all the chemicals listed in the Merck Index, the resulting mixture would look something like chocolate and smell something like chocolate, although it probably wouldn't taste anything like chocolate (and you wouldn't want to eat it).*

The point is that the flavor of chocolate comes from a complex mixture of numerous different chemical components, with an estimated number of over 600 or so different chemicals associated with chocolate flavor. The main chemical classes involved with chocolate flavor include pyrazines, esters, amines and amides, acids, and hydrocarbons, although numerous other chemical classes (alcohols, aldehydes, furans, ketones, pyridines, pyrons, pyrroles, and sulfur compounds) have been identified in chocolate flavor (Counet et al. 2002; Aprotosoaie et al. 2015; Tran et al. 2015; Kongor et al. 2016). Aprotosoaie et al. (2015) provide a summary of both desirable and undesirable aroma compounds often found in chocolate. Some of these components may be present at only the parts per million level, yet still have a profound influence on perceived flavor. The polyphenols and alkaloids present in chocolate also affect flavor, primarily through their bitter characteristics.

Not only is the chemical composition of chocolate flavor incredibly complex, the variety of factors that can influence chocolate flavor is also extremely broad. From the nature of the beans and how they are treated to the operating conditions used in the various process steps needed to make chocolate, there are an incredible number of opportunities to influence chocolate flavor. Because of this complexity, only brief highlights of flavor development in chocolate are provided here. Further details can be found in reviews of flavor development in chocolate (Ziegleder 2009; Kongor et al. 2016).

The first opportunity to select or influence flavor comes in the choice of bean itself. The species, origin and even climate during growth affect the chemical make-up of the bean and influence its flavor. Criollo beans, making up only a few percent of commercial production, are considered to have the finest chocolate flavor, with a mild nutty flavor and low chocolate intensity, low bitterness and astringency. In contrast, the remaining broad group of cocoa beans have many different flavor profiles. They have a stronger chocolate flavor, more bitterness and astringency with much variance in the amounts of fruity and floral notes. Like wine or coffee, certain regions or locales become known for signature flavors and are purchased for these characteristics. Often, beans from different sources are blended to produce specific characteristics in chocolate flavor.

Once the beans have been harvested, the fermentation process has a significant impact on flavor profile through the combination of fermentation processes and enzymatic reactions (see Section 15.2.1). The conversion of chemical components present in the raw bean to flavor precursors during fermentation is critical to subsequent flavor development in later processing steps. Of the numerous changes that take place during fermentation, several are of critical importance to subsequent flavor development during roasting, where the Maillard browning reaction predominates. The hydrolysis of sucrose into glucose and fructose provides reducing sugars and proteolysis produces peptides and free amino acids, both reactants needed in the Maillard reaction. Unfermented beans are deficient in these substrates and thus, do not develop good chocolate flavors upon roasting. Other contributions to chocolate flavor during fermentation include the degradation of polyphenols, which reduces the astringent character of chocolate, and acid production, particularly acetic and lactic acids. Bacterial production of organic acids during fermentation reduces the pH and shuts down enzymatic reactions within the first few days of fermentation.

As a continuation of some of the reactions that occur during fermentation, the drying step also can have significant impact on flavors. Some residual enzyme activity occurs during drying, but the warm temperatures of drying lead to initiation of the Maillard browning. Although the reaction does not proceed far enough to generate characteristic chocolate flavor, some of the early products (Amadori compounds) of the reaction between glucose/fructose and free amino acids are generated. These either decompose during roasting or continue along the Maillard browning pathway to generate characteristic flavors.

In the manufacturing plant, numerous processing steps bring out the flavors inherent in the cocoa bean. Primary of these is roasting, where time and temperatures are major factors (think ‘French’ roast, etc.) along with the type of roaster used. Differences in flavor development also occur based on which material (cocoa beans, nibs or chocolate liquor) is roasted and any other pretreatments that may have been used.

During roasting, Maillard browning (predominant) and other thermolysis reactions occur that contribute to the overall chocolate flavor. Maillard browning is a complex series of steps in which reducing sugars and proteins are converted into various flavor and color compounds (see Sections 1.2.2.1 and 10.4.1). Numerous factors affect the specific compounds produced during Maillard browning. These include, but are not limited to, pH, temperature and time, substrate materials, and water content.

Alkalization (or Dutching) also affects chocolate flavor. The higher pH caused by alkalization increases the rate of the Maillard browning reaction, and also alters the relative extent of the different reaction pathways. This leads to different colors and aromas being generated upon roasting. Alkalization gives a less acidic flavor with 'fudgey' or 'brownie' notes. It also degrades/destroys flavanols, thereby reducing bitterness and astringency of the final product.

Conching is the last major step of processing where chocolate flavor can be influenced. Time, temperature, air flow and degree of shear all can significantly affect final flavor development. It is generally thought that removal of certain flavor compounds and acids by volatilization during shear mixing in the conch helps to smooth out chocolate flavor. However, certain types of off-flavors (i.e., smoky or moldy) cannot be removed in the conching process. During dry conching, the chocolate mass is sheared continuously to expose new surfaces with air; this allows rapid volatilization of certain flavorant molecules. For example, the acetic acid level in the chocolate paste decreases during conching, which decreases bitterness and perhaps allows the other chocolate flavors to come through more clearly. Counet et al. (2002) quantified the effects of conching on the levels of over 80 different key odorants found in dark chocolate. Most of these flavor compounds decreased during conching, although several actually increased in concentration. While conching is generally equated with the removal of flavors, high temperature conching can cause the development of caramelized flavor notes.

The addition of dairy ingredients to milk chocolate moderates chocolate flavor and further, the choice of milk processing technique also has a major effect on chocolate flavor. As noted in Section 15.4.7, the removal of water in milk to allow its incorporation into chocolate requires heat, which subsequently changes milk flavor compounds. The method of water removal, whether by evaporating to make milk powder or kneading with sugar to make milk crumb, determines the nature of these milk flavors.

Adding to this chemical complexity, the manner in which chocolate components interact in the mouth also affects flavor and aroma of chocolate during consumption. Dissolution of sugar and melting of fat influence the release of volatile flavors sensed by the olfactory organ at the same as these physical phenomena influence the mouthfeel characteristics. The relative volatility and diffusion rates of the various components and their partitioning between chocolate (oil-based), saliva (water-based) and air determine how each of the components is sensed. Even the particle size (sugar, cocoa, milk powder) can influence flavor perception, with smaller particles giving a more milky flavor while chocolates with larger particles are perceived to be more sweet.

15.8.2 Polyphenols and Flavanols in Cocoa and Chocolate

Much recent work has gone into quantifying and categorizing the polyphenol content of chocolate products due to the potential health effects. Raw beans contain about 15% soluble polyphenols on a fat-free, dried bean basis.

Proanthocyanadins make up the largest class of polyphenols (ca. 58%), with catechins or flavan-3-ols making up most of the rest (ca. 37%). In Forastero beans, anthocyanins (ca. 4%) are also found. The predominant flavan-3-ol in cocoa beans is (–)-epicatechin. Table 15.7 lists the polyphenols that have been found in cocoa beans or cocoa-related products.

The high polyphenol content in raw cocoa beans decreases substantially during processing into chocolate. However, since polyphenols generally have a bitter characteristic, this degradation in polyphenols has traditionally been considered advantageous. As described in Section 15.2.1, fermentation is the first processing step where significant degradation of polyphenols occurs. Epicatechin and soluble polyphenol content decrease considerably (Kim and Keeney 1984; Wollgast and Anklam 2000; Payne et al. 2010) due to both oxidation (enzymatic and nonenzymatic) and drip loss of the water soluble polyphenols out of the fermentation pile. Anthocyanins also decrease substantially during fermentation. They are initially

Table 15.7 Polyphenols identified in cocoa or cocoa-related products

Class	Specific polyphenols
Catechins	(−)-epicatechin
	(+)-catechin
	(+)-gallocatechin
	(−)-epigallocatechin
Procyanidins	Procyanidin B1 – epicatechin-(4β—8)-catechin
	Procyanidin B2 – epicatechin-(4β—8)-epicatechin
	Procyanidin B3 – catechin-(4β—8)-catechin
	Procyanidin B4 – catechin-(4β—8)-epicatechin
	Procyanidin B5 – epicatechin-(4β—6)-catechin
	Procyanidin C1 – epicatechin-(4β—8)-epicatechin-(4β—8)-epicatechin
	Procyanidin D – epicatechin-(4β—8)-epicatechin-(4β—8)-epicatechin-(4β—8)-epicatechin
	Higher oligo- and polymers, mostly homologues of epicatechin with 12–18 monomeric units
Anthocyanins	Cyanidin-3-α-L-arabinosid
	Cyanidin-3-β-D-galactosid
Flavanol glycosides	Quercitin-3-*O*-α-D-arabinosid
	Quercitin-3-*O*-β-D-glucopuranosid
Others	Clovamide
	Dideoxyclovamide

Adapted from Wollgast and Anklam (2000)

hydrolyzed to anthocyanidins, which further react to form complex tannins. Anthocyanin loss is nearly complete during fermentation, with 93% loss after 4 days of fermentation (Wollgast and Anklam 2000). For this reason, anthocyanin content has been used as an indicator of extent of fermentation of the cocoa bean.

Subsequent processing of the cocoa bean into chocolate involves numerous steps where polyphenol content can be further reduced. Alkalization or Dutch processing substantially reduces the levels of flavanols in chocolate liquor or cocoa powder. Alkalization of the powder or chocolate mass to pHs slightly over seven reduces the flavanol levels in cocoa powders by about 60% compared to untreated material. Additional alkaline treatment with higher pHs, higher heats and/or longer times can reduce the flavanol content by 90% (Miller et al. 2008). Interestingly nonalkalized cocoa powder also loses substantial flavanol content in brownie and cake recipes made with baking soda, a strong base, compared to the same recipes made with baking powder, which is slightly acidic (Stahl et al. 2009).

Roasting (see Section 15.4.4) also causes significant changes in polyphenols (Payne et al. 2010). Here, high temperatures induce chemical reactions that lead to chocolate flavor development, but these high temperatures also cause further degradation of polyphenols, with losses estimated to be about 75% in Ivory Coast beans and about 45% in heavily fermented Papua New Guinea beans. Temperature of roasting is a critical parameter, with higher temperatures leading to greater degradation (Payne et al. 2010). Roasting time is also an important parameter, with longer roasting times leading to lower levels of polyphenols. In general, lightly roasted beans retain significantly more of the polyphenols than dark-roasted beans.

Polyphenols are typically not oil soluble, so the cocoa butter phase of chocolate contains little if any polyphenol content. Thus, when cocoa butter is pressed out of chocolate liquor, the resulting cocoa powder is concentrated in polyphenols, with natural (nonalkalized) powders containing perhaps 4–5% total flavanols. Payne et al. (2010) characterized the effects of Dutch processing (alkalization) on catechin and epicatechin content. Epicatechin level decreased nearly linearly with pH, from 2.25 mg/g at natural pH (5.6) to 0.04 mg/g for heavily alkalized cocoa (pH 7.9).

It is clear that processing of cocoa beans into chocolate liquor causes a significant reduction in flavanol content. Payne et al. (2010) show the decrease in epicatechin from 16 mg/g in unripe beans to less than 1 mg/g in roasted beans, depending on the extent of roasting. Higher roasting temperatures, not surprisingly caused greater decreases in epicatechin levels. Further formulation components (e.g., adding sugar or other ingredients) decrease epicatechin levels even further, resulting in finished chocolate products with a wide range of flavanols (Alanon et al. 2016).

Alanon et al. (2016) measured flavanol content in numerous commercial chocolates, both milk and dark. Total flavanol levels varied from as low as 0.095 to as high as 3.62 mg/g of chocolate, although milk chocolates had on average lower total flavanol content (0.710 mg/g average with a low of 0.202 and high of 2.237 mg/g) than dark chocolate (1.173 mg/g average with low of 0.05 and high of 3.624 mg/g). Epicatechin content in milk chocolates averaged 0.239 mg/g with low of 0.085 to a high of 0.637 mg/g, whereas for dark chocolate the average was 0.337 mg/g with low of 0.038 to high of 0.807 mg/g. These results clearly show the range of flavanol/epicatechin content and that one cannot assume that a milk chocolate will have lower flavanol/epicatechin content and that dark chocolate will always have the higher level. Each of the factors discussed above influence the final flavanol levels. Further, the correlations with calculated percent cacao were poor, indicating that the claim of "% cacao" on a label is not necessarily a good indicator of polyphenol/epicatchin content in a chocolate.

Since flavanol content in chocolate stems primarily from the amount of cocoa particles contained in the chocolate, it is no surprise that good correlations with nonfat cocoa solids have been found in commercial products (Miller et al. 2006, 2009). Total polyphenols and total procyanidins exhibited excellent linear correlations (R^2 values >0.94) with nonfat cocoa solids in a wide range of chocolate products available in the United States market (Miller et al. 2006). Catechin and epicatechin content also exhibited strong linear correlations with nonfat cocoa solids, but with slightly lower correlation coefficients, suggesting that other factors were also involved (Miller et al. 2009).

Based on these results, some general strategies to make chocolate products with high levels of polyphenols and flavanol emerge, although each has its own trade-offs. First, since cocoa beans vary widely in their polyphenol content, selecting beans with the highest initial levels of polyphenols and flavanols will ensure that more of these bioactives will be in the finished chocolate. Reducing fermentation time will reduce the amount of degradation that takes place. Slightly under-fermented beans retain more of the desirable polyphenols as do slightly under-roasted beans (lower temperature and reduced time of roasting). In general, a high cocoa chocolate, not alkalized, with less sugar and milk ingredients retains the highest level of polyphenols. Unfortunately, chocolate with higher levels of polyphenols also tends to be more bitter and astringent.

15.8.3 Chocolate Rheology

The ability of melted chocolate to flow under shear forces (i.e., pumping, enrober curtain, stirring, pouring, etc.) is a very important physical characteristic since the rheological properties ultimately determine the most suitable application for a specific chocolate. In order to understand the factors that influence chocolate rheology and what this means to the applications of chocolate, the principles of fluid flow under shear forces must first be understood. Specifically, fluids undergo internal frictional forces as molecules and/or physical structures (i.e., particles, emulsion droplets, air bubbles, etc.) are forced to flow past each other in a shear field (that is, in flow with a velocity gradient). The nature of those forces under shear flow is the basis of the field of rheology. Section 2.2 discusses rheological principles as related to sugar solutions, but here that discussion is expanded for chocolates.

In melted chocolate, the rheology is governed by the combination of the liquid cocoa butter and the particulate dispersion, which makes chocolate rheology much more complex than sugar solutions. Melted chocolate is a dispersion of small cocoa solid particles and sugar crystals surrounded by the liquid fat phase, cocoa butter. In milk chocolates, milk powder particles may also be found, depending on the manufacturing method (see Section 15.4.7.1) and milk fat contributes to the fat phase. The particles in chocolate vary in size from less than 1 μm to as large as

30 to 40 μm, although most particles fall in a narrow range between 10 and 20 μm. Since the cocoa butter content is typically between 30% and 35%, the particulate dispersion in chocolate, making up 65–70% by weight, contributes significantly to the rheological properties of melted chocolate. When liquid chocolate is sheared, the particles rolling across each other create a type of friction that reduces the ability to flow. This can be better understood by comparing chocolate to pure cocoa butter and water. Pure water contains small molecules that have no problem flowing across each other under shear forces. Thus, the viscosity, or resistance to flow, for water is very small. Similarly for pure liquid cocoa butter, the resistance to flow comes from the friction of cocoa butter triglycerides moving across each other. Like water, this resistance is relatively low and thus, the viscosity of pure molten cocoa butter is also quite low. In contrast, the ability of melted chocolate to flow under shear is severely restricted by the large number of small particles. On all sides, each particle is forced to interact with numerous other particles as chocolate is sheared and thus, melted chocolate has a very high viscosity compared to water. The irregular shape of the particles in chocolate also contributes to the viscosity effect. Smooth spheres interact to a much less extent than the irregular fractured particles of sugar and cocoa solids. Any chemical or electrostatic interactions between particles further enhance the viscosity increase caused by particles in close proximity.

These particulate interactions lead to the phenomenon of thixotropic, or time-dependent, behavior in melted chocolate. After sitting for a while with no stirring, these interactions build among the particles. When the chocolate is freshly stirred, these interactions induce an artificially high viscosity, which decreases over time as the interactions are broken, until the melted chocolate reaches a steady-state viscosity characteristic of the applied shear rate, as shown schematically in Figure 15.16. The standard method of measuring chocolate viscosity requires a preshearing period, specifically intended to eliminate any time-dependent behavior so the steady-state viscosity can be measured.

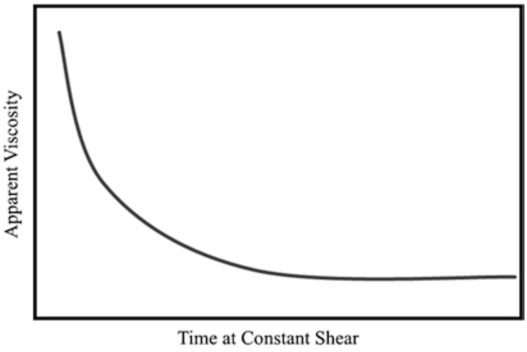

Figure 15.16 Schematic of time dependent, thixotropic, behavior of melted chocolate

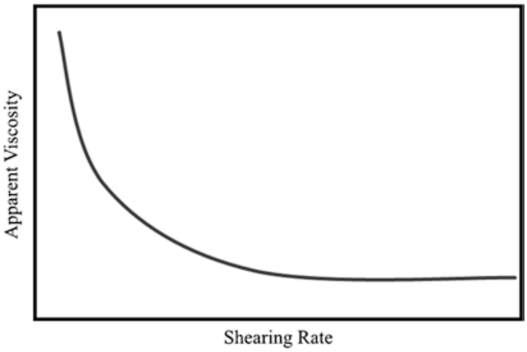

Figure 15.17 Chocolate as a shear-thinning fluid: decrease in apparent viscosity of melted chocolate with increase in shearing rate

To further complicate chocolate rheology, the nature of the interactions among particles depends on the shearing conditions (Windhab 2006). At low shear rates, the extensive particle interactions create high friction and adhesion forces, so that the viscosity is high. As shearing forces increase, the particles reorient themselves and network structures are broken, resulting in a greater ability to flow. This leads to a lower viscosity. A melted chocolate under very slow stirring speeds has higher apparent viscosity compared to that same chocolate measured at higher stirring speeds. That is, chocolate also behaves as a shear thinning fluid, where it is apparently less viscous at higher shearing rates. This is shown schematically in Figure 15.17. In general, the more intense the shearing (agitation, pumping, etc.) of chocolate, the lower the apparent viscosity.

Also, due to their surface characteristics, many of the particles in chocolate tend to form weak aggregates. For example, the hydrophilic nature of sugar particles means that sugar crystals would rather interact with each other than with the cocoa butter in which they are contained. This combination of particulate proximity and weak aggregation make the chocolate initially difficult to stir, pump or pour. Yield stress is the force required to break these structures and initiate flow in the melted chocolate.

Melted chocolate is a complex material that exhibits both shear-thinning (also called pseudo-plastic) behavior and a yield stress. These rheological parameters have been defined according to the Casson model of rheology (Seguine 1988), which correlates the shear stress (or force applied per unit area), σ, with the resulting velocity profile, or shear rate, γ, according to Equation 15.1.

$$\sqrt{\sigma} = \sqrt{\sigma_c} + \sqrt{\eta_c}\sqrt{\dot{\gamma}} \qquad (15.1)$$

The parameters that define the rheological properties are yield stress, σ_c, and plastic viscosity, η_c. Figure 15.18a schematically shows the relationship between shear stress and shear rate for chocolate. The yield stress is the force (per unit area) required to initiate flow, with thicker chocolates generally needing higher initial forces to initiate flow (Afoakwa et al. 2009a).

The Casson plastic viscosity is related to the consistency or thickness of the chocolate, with thicker chocolates having higher plastic viscosity. As a shear thinning fluid, the thickness, or apparent viscosity, of melted chocolate decreases as the rate of shearing increases, as seen in Figure 15.17. The apparent viscosity, η_a, is defined as the ratio between shear stress and shear rate, as seen in Equation 15.2 for the Casson model of chocolate rheology.

$$\eta_a = \frac{\sigma}{\dot{\gamma}} = \frac{\left\{\sqrt{\sigma_c} + \sqrt{\eta_c}\sqrt{\dot{\gamma}}\right\}}{\dot{\gamma}} \qquad (15.2)$$

Accordingly, the apparent viscosity of a fluid that follows the Casson model decreases with increasing shear stress with a complex functionality. Apparent viscosity is high at low shear conditions and becomes increasingly lower as shear rate increases.

To measure the Casson viscosity parameters for chocolate, a viscometer is required (Seguine 1988). The standard viscometer recommended for chocolate by the National Confectioners Association in the United States consists of two concentric cylinders between which is the chocolate, with the inner cylinder rotating and the outer cylinder stationary (Figure 15.19). The inner cylinder is attached to a load cell in the unit's housing. As force is applied to the chocolate by rotating the inner cylinder at a set rotational speed (RPM), the chocolate applies a force back on the inner cylinder, which is read as the torque on the load cell. In this way, the concentric cylinder provides the correlation between shear rate

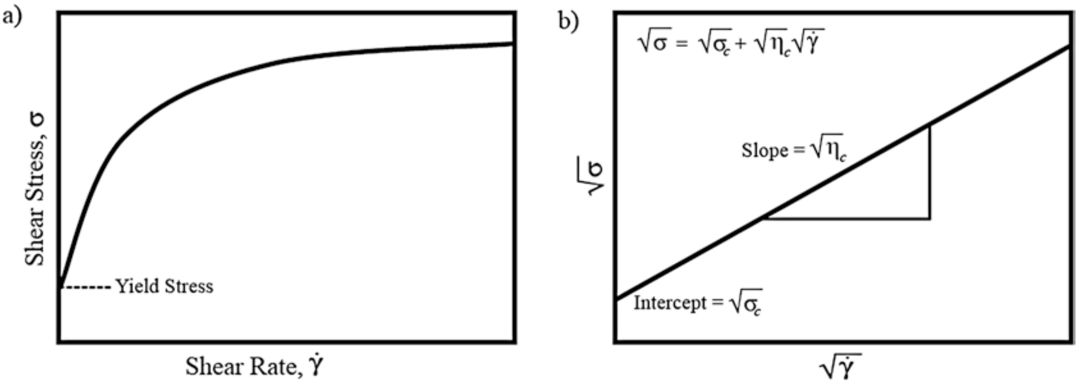

Figure 15.18 Relationship between shear stress (σ) and shear rate (γ) for melted chocolate: (**a**) shear thinning behavior with yield stress (σ_c); (**b**) Casson model

Figure 15.19 Concentric cylinder rotational viscometer used for measuring rheological properties of chocolate (Courtesy of Brookfield)

(RPM) and shear stress (torque) required for the Casson model.

To obtain the Casson parameters from the rotational viscometer data, there is first a preshearing step to destroy any time-dependent (thixotropic) flow behavior. The RPM of the spindle is then set to a specific value and the torque value measured after a set period of time (or spindle rotations). Typically, spindle RPM is increased (ascending mode) and then decreased again (descending mode) to ensure that there is no hysteresis in measurement, where changing shear rate causes a change in response. Hysteresis could potentially occur if the chocolate was not presheared properly or if it was not conched completely and the shear forces during measurement actually caused de-agglomeration of particles.

Once shear rate and shear stress data have been collected, the Casson model (Equation 15.1) is linearized (by taking the square root) and regression analysis performed to obtain slope and intercept. Figure 15.1b shows the linearization. The Casson plastic viscosity, η_c, is obtained from the square of the slope and the Casson yield stress, σ_c, obtained from the square of the intercept. More details, including further refinements of the method and the constraints under which data should be obtained from a concentric cylinder viscometer, can be found in the description by Seguine (1988).

The Casson parameters are used to guide the proper application. Chocolates intended for use in filling molds with complex and intricate designs must have low yield stress and low viscosity so they flow easily into all crevices to completely fill out a design. On the other end of the spectrum are the chocolates that form chips or drops as they are deposited on conveying belts. These chocolates need high viscosity and high yield stress so that once deposited, no further flow is possible and they retain their shape. The high yield stress of these chocolates prevents the melted chocolate from flowing out into a thin puddle. Figure 15.20 shows the range of rheological properties recommended for different chocolate applications.

Although the Casson model is widely used, many chocolate scientists feel that it does not fully and adequately describe the rheological properties of chocolate. Aside from the errors associated with extrapolating a yield stress from shear stress versus shear rate data, the difficulty in obtaining reproducible data among different analysts has led to alternative methods of characterizing chocolate rheology. For example, Servais et al. (2004) proposed a three-point approach to characterizing chocolate rheology. They suggest measuring the shear stress at a shear rate of 5 s^{-1} to represent yield stress, the shear stress at a shear rate of 40 s^{-1} to represent viscosity at high shear (pumping), and the difference between viscosity measured at 40 s^{-1} on a ramp up versus a ramp down analysis to characterize the thixotropic (time-dependent) behavior of chocolate. The claim is that this approach gives more reproducible results with a simpler analysis and that this approach gives parameters that are more pertinent to chocolate processing than the Casson model. Do et al. (2007) use a version of this approach to compare rheological properties of model chocolate systems.

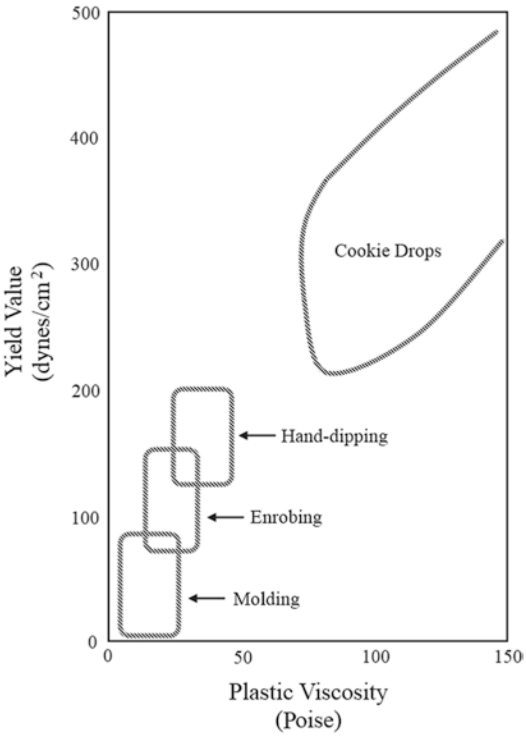

Figure 15.20 Yield stress and plastic viscosity requirements for different chocolate applications (Courtesy of E. Seguine)

Although the Casson model and these other more sophisticated scientific approaches give a complete description of the rheological properties of melted chocolate, it is more common, particularly in quality control departments, to use a single point measurement for chocolate viscosity. A sample of melted chocolate is placed in the viscometer, as described previously, and a viscosity reading obtained (usually at shear rate of 20 s^{-1}). This value, given in centiPoise (cP), is used to ensure that chocolate meets the viscosity specification set for that product. In fact, this single point measurement of chocolate viscosity is used widely to characterize chocolate flow behavior, with no reference to the more complete Casson parameters.

15.8.3.1 Factors Affecting Chocolate Rheology

Although the complex rheological behavior of chocolate is due in large part to the particulate nature of chocolate, the nature of the liquid fat can also have a significant effect. Thus, both aspects are discussed here. The characteristics of the particles that can influence the rheological properties include the amount of particulate phase, particle size and distribution, and surface characteristics and modifications (e.g., emulsifier addition) (Windhab 2006). The nature of the lipid phase, both the amount of fat present and the nature of that fat, can also affect rheological properties. The content of surface-active lipids, whether added specifically as emulsifier or present naturally in the fat, also affects rheological properties through their effect on the particulate interfacial properties. Afoakwa et al. (2007) review the different factors that influence the rheological properties of chocolate.

The fat content of chocolate determines the mass fraction of particulates, which governs the proximity of those particles to each other. Specifically, as fat content increases, the distance between particles increases and their interactions during shear decrease. Thus, higher fat content in chocolate leads to lower viscosity, both in terms of yield stress and plastic viscosity. An increase in fat content from 28% to 32%, for example, can cause a twofold reduction in yield stress and a two to sixfold decrease in plastic viscosity depending on particle size.

It is well known that viscosity and yield value decrease as particle size increases. The lower surface area of larger particles means that less cocoa butter is needed to keep them separated during flow. However, the distribution of sizes and not just the mean size also affects chocolate rheology. During refining, the particulate material in chocolate is fractured, chipped or abraded to create smaller and smaller particles. If abrasion is the primary mechanism of breakage, numerous small particles will be produced, with many of these particles being less 5 μm in size. These very small particles, with huge surface area, are thought to cause a significant increase in viscosity because they need higher amounts of fat to "coat the surface". As noted by Ziegler and Hogg (2009), this probably oversimplifies the situation. Not only does total surface area of particulates affect rheological properties, the manner in which the particles pack together (e.g., packing density) also affects viscosity (Mongia and Ziegler 2000; Do et al. 2007). Recent advances in our understanding of the effects of particulates on chocolate rheology have the potential to lead to manufacture of reduced fat chocolate products that retain sufficiently low viscosity for processing and the desired melt-down properties in the mouth.

The shape of the particles can also greatly impact rheological properties, particularly irregularly shaped sugar crystal fragments. When the surface of these irregular sugar crystals has been smoothed through a water treatment (St. John et al. 1995), viscosity is greatly reduced. This allows production of a chocolate with reduced fat (as low as 20%) that still retains sufficiently low viscosity that it can be processed and still melts in the mouth.

The surface characteristics of the particles in chocolate can have a strong effect on rheological properties. In fact, emulsifiers like lecithin and PGPR (polyglycerol polyricinoleate) are added to chocolate specifically for their effects on rheological properties of chocolate. A few tenths of a percent of lecithin added to liquid chocolate at the end of conching causes a significant reduction in apparent viscosity. Since cocoa butter is a costly component of chocolate, the savings observed with use of low levels of lecithin are significant. Lecithin imparts this viscosity reduction primarily through its interaction at the surface of the sugar particles. Sugar crystals are a hydrophilic (or lipophobic) material, meaning the particle surfaces would prefer to interact with other sugar particle surfaces rather than with the cocoa butter. Lecithin migrates to the surface of the sugar particles where the hydrophilic head group interacts with the surface while the fatty acid chains of lecithin interact with the cocoa butter (Kindlein et al. 2015). In this way, a coating of lecithin prevents sugar particles from interacting with each other, easing their motion across each other during shearing.

However, addition of more than about 0.5% lecithin can cause the apparent viscosity of chocolate to increase. This increase in apparent viscosity is due primarily to an increase in yield stress, with little to no change in plastic viscosity at lecithin levels up to 1%. The mechanism for this increase in yield stress at high lecithin levels has not been clearly established although the effects are thought to be related to either additional structures being formed (e.g., lecithin micelles) or a decrease in the surface-coating efficiency of lecithin. Formation of multi-layers of lecithin around the sugar particles may also promote bridging of particles that would otherwise be easily separated.

Addition of low levels of PGPR causes yield stress to go essentially to zero (Rector 2000; Schantz and Rohm 2005; Weyland and Hartel 2008), suggesting that it acts at the particle interface to completely eliminate any interactions among particles. This decrease in yield stress comes with almost no effect on plastic viscosity. Chocolates intended for molding, particularly into fine printed designs, benefit greatly from the yield stress reduction that PGPR brings.

Added emulsifiers are not the only source of surface-active lipids in chocolate. All natural fats contain polar lipids, such as mono- and diglycerides (MAG/DAG), phospholipids and sterols, which have their own inherent surface-active properties. Natural fats may contain up to 2–3% of these components, but processing such as deodorization may decrease this level. Deodorization is used to provide a cocoa butter with a mild neutral flavor. Minor lipid components of various cocoa butters from different origins are shown in Table 15.8. Considerable variation exists among different cocoa butters, due in part to differences in processing, but also due in part to natural variations in raw materials from different origins. These differences in minor chemical components can potentially lead to significant differences in crystallization rates, bloom stability, and physical properties, such as viscosity. Babin et al. (2005) studied the effects of various surface-active components, both added and inherent, on sedimentation volume and apparent viscosity of sugar particles in cocoa butter. When the polar lipids naturally present in cocoa butter were removed, there was very little effect on sediment volume and apparent viscosity, unlike the effects found with other oils (e.g., palm kernel oil). That is, removing the minor lipid impurities from cocoa butter did not significantly affect rheological prop-

Table 15.8 Minor lipid composition of cocoa butters from various origins

	W. African	South American			
Component	Ivory Coast	Ecuador	Bahia	Columbia	Malaysian
FFA[a]	2.13	0.77	1.62	1.06	1.59
MAG[a]	0.02	0	0.06	<0.01	0.02
DAG[a]	1.67	1.41	2.01	1.04	2.05
Sterols[b]					
Total	2069	1989	1912	2061	1968
Cholesterol	28	20	24	26	28
Campestrol	176	148	162	180	173
Stigmasterol	565	520	521	541	515
Cleresterol	17	11	14	13	15
Sitosterol	1104	1154	1045	1163	1068
D5 Avanasterol	53	37	47	44	59
D7 Avanasterol	52	13	20	19	31
D7 Stigmasterol	13	13	18	16	17
D5, D24 stigmasterol	61	64	61	59	62
Phospholipids[c]					
Total	45.3	33.0	42.4	37.5	81.5

Courtesy of A. Lechter

[a] *FFA* free fatty acids (%), *MAG* monoglycerols (%), *DAG* diacylglycerols (%)

[b] mg/kg

[c] mg Phosphorous/kg

erties, suggesting that these components are not as surface active as in some other oils. However, the addition of lecithin was observed to decrease apparent viscosity of the sugar dispersion in cocoa butter, as expected, and to a much greater extent than for glycerol monostearate (GMS). Although Babin et al. (2005) found no effects of cocoa butter minor lipids on viscosity, these components may still influence crystallization behavior and bloom stability (Tietz and Hartel 2000).

Other materials that may be added to chocolate, intentional or otherwise, can also potentially increase viscosity. When small amounts of water (even as small as 0.5%) are added to chocolate, a large increase in viscosity is soon apparent. This fact can be useful to suspect microscopic water leaks with jacketed processing equipment. Even moisture uptake into chocolate during storage can cause a gradual increase in viscosity when the chocolate is re-melted. In like manner, flavorings that contain water, glycerol, alcohols, or other hydrophilic solvents may also increase chocolate viscosity.

15.8.4 Melting Profile

The melting properties of chocolate depend primarily on the nature of the fat phase although the nature of the particulate dispersion can also affect flow properties upon melting. This is important both during processing and consumption.

Cocoa butter in chocolate has a somewhat unique melting profile for a natural fat (Chapter 4). As seen in Figure 15.21, it is quite hard at room temperature, has a relatively sharp melting curve between 25 and 34 °C (77–93 °F), and is completely melted at normal mouth temperature of about 35 °C (95 °F). The high solid fat content (SFC), from 75% to 90% crystalline fat, of cocoa butter at room temperature provides chocolate with a solid-like characteristic and the unique snap. The many small cocoa butter crystals formed during proper tempering and cooling provide a matrix of crystallized fat around the particulate mass (sugar crystals, cocoa solids, milk particles) that sets into a hard matrix.

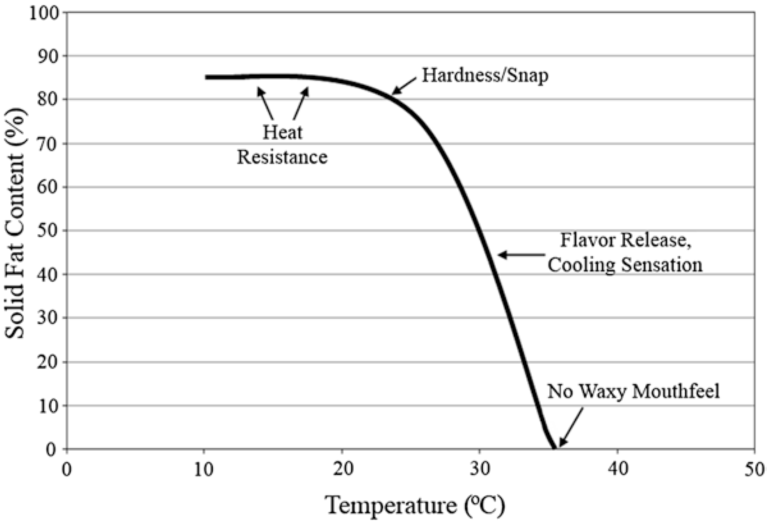

Figure 15.21 General melting profile of cocoa butter

As temperature increases above room temperature, more and more of the crystalline triglycerides melt and the chocolate becomes softer. Within about a 10 °C (18 °F) range, cocoa butter goes from mostly solid and crystalline to mostly melted and fluid. This relatively sharp (relative to many natural fats) melting profile provides a unique eating experience, accompanied by intense flavor release. A moderate cooling effect also occurs as the latent heat needed for melting the cocoa butter molecules is removed from the environment (in the mouth). Ideally, the last cocoa butter crystals melt in the mouth of the consumer, leaving behind no trace of solid fat prior to swallowing. If for some reason, a portion of the cocoa butter remains crystalline in the mouth, the consumer is likely to perceive the chocolate as waxy since the fat remains solid in the mouth and must be chewed.

Since cocoa butter is a natural product, there is significant variation in composition based on cacao origin. Tables 15.9 and 15.10 show the different fatty acid and TAG distributions, respectively, for several cocoa butters from different origins. Based on these compositional differences, the melting properties are different for cocoa butters from different growing regions (Figure 15.22). Typically, cocoa butter from Indonesia and Malaysia is known to be harder and crystallize more rapidly than cocoa butter from South America (e.g., Brazil), with West African cocoa butters having intermediate melting point and crystallization rates (Chaiseri and Dimick 1989). Differences in hardness and melting properties are primarily related to the relative composition of the different cocoa butters. Softer South American cocoa butters on average have slightly less diunsaturated triglycerides, SOO and POO (S-stearic, P-palmitic, O-oleic) than the harder Indonesian/Malaysian cocoa butters (Chaiseri and Dimick 1989). West African cocoa butters fall between the South American and Asian/Oceanic cocoa butters in SOO/POO content and hardness. Iodine values (IV) among the different cocoa butters are only slightly different, with South American cocoa butters having slightly higher IV (37.04) than the Asian/Oceanic cocoa butters (34.7) (Chaiseri and Dimick 1989).

Hardness and snap of chocolate can also depend on the composition of the lipid phase. For example, the differences in snap between dark chocolate and milk chocolate are due to the phase behavior of the lipids. The mixture of milk fat with cocoa butter causes eutectic softening, resulting in reduced solid fat content. The result is that milk chocolate is softer than dark chocolate. In fact, some chocolate manufacturers add up to a few percent of anhydrous milk fat to dark chocolate to moderate the hardness of cocoa butter to make a slightly softer dark chocolate with more flavor release.

Table 15.9 Fatty acid (%w/w) distributions for cocoa butters from various origins

	W. African	South American			
Fatty acid	Ivory Coast	Ecuador	Bahia	Columbia	Malaysian
Myristic C14:0	0.12	0.08	0.10	0.095	0.105
Palmitic C16:0	25.90	28.01	26.95	27.11	25.09
Palmitoleic C16:1	0.29	0.31	0.30	0.28	0.26
Stearic C18:0	36.19	32.61	34.40	33.50	36.68
Oleic C18:1	31.97	33.07	32.52	33.19	32.40
Linoleic C18:2	2.92	3.48	3.20	3.26	2.73
Linolenic C18:3n3 *cis*	0.21	0.24	0.22	0.23	0.22
Arachidic C20:0	1.16	0.98	1.07	1.09	1.25
Gadoleic C20:1n9 *cis*	0.06	0.06	0.06	0.06	0.07
Behenic C22:0	0.22	0.19	0.20	0.22	0.23
Lignoceric C24:0	0.13	0.13	0.13	0.12	0.15

Courtesy of A. Lechter

Table 15.10 Triacylglcerol (TAG) distributions (% w/w) for cocoa butters from various origins

	W. African	South American			
TAG[a]	Ivory Coast	Ecuador	Bahia	Columbia	Malaysian
PPP	0.10	0.10	0.05	0.09	0.11
MOP	0.13	0.11	0.10	0.09	0.10
PPS	0.49	0.41	0.27	0.40	0.53
POP	14.51	17.08	13.52	15.94	13.70
PLP	1.77	2.64	2.26	2.18	1.62
PSS	0.79	0.53	0.45	0.55	0.82
POS	38.57	37.55	34.21	37.45	37.56
POO	1.56	3.01	4.93	2.82	1.87
PLS	4.08	4.74	4.48	4.27	3.66
PLO	0.38	0.49	0.81	0.61	0.28
SSS	0.44	0.24	0.23	0.28	0.47
SOS	28.43	23.17	24.14	24.85	29.28
SOO	2.38	3.87	7.02	3.87	2.93
SLS	2.47	2.41	2.39	2.34	2.38
OOO	0.18	0.37	0.66	0.29	0.27
SLO	0.32	0.54	1.02	0.51	0.26
SOA	3.40	2.46	2.72	3.00	3.78
AOO	0.00	0.28	0.73	0.45	0.39

Courtesy of A. Lechter

[a] *M* myristic, *P* palmitic, *S* stearic, *O* oleic, *L* linoleic, *A* arachidic

Melting of chocolate is not only related to the nature of the fat, but also depends on the particulate material (Do et al. 2007). An increase in fat content (decrease in solids content) was found to reduce the time necessary for onset of melting, due primarily to the differences in thermal conductivity between fat and particulate solids. Fat, with a higher thermal conductivity, warmed up faster and began to flow more quickly. The rate of collapse, associated with chocolate melting,

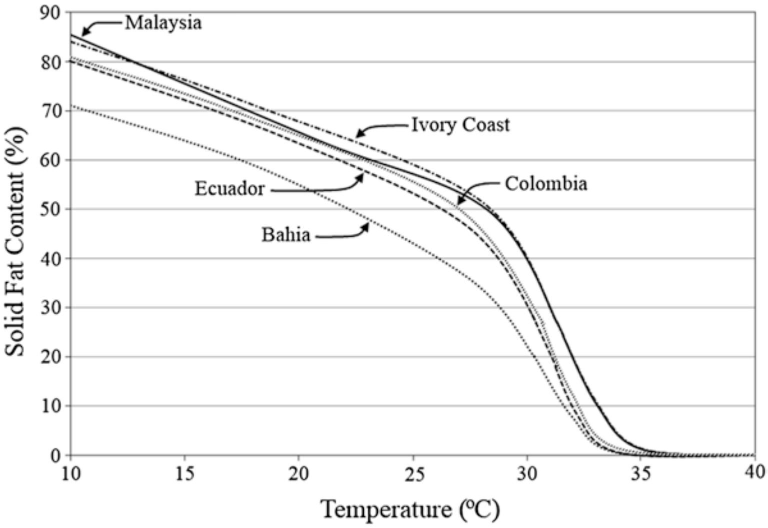

Figure 15.22 Melting profiles for cocoa butters from different countries of origin (see Tables 15.9 and 15.10 for corresponding compositional data) (Courtesy of A. Lechter)

generally increased with increasing fat content, but the effect was moderated by particle size. Larger particle size led to a faster rate of collapse due to the reduction in particle aggregation and friction as the fat melted, allowing flow to occur more readily. Smaller particles slowed collapse due to the frictional forces and interactions among the particles.

15.8.5 Crystallization, Polymorphism and Tempering

Each cocoa butter crystallizes in a slightly different manner based on its inherent chemical composition (both triglycerides and minor lipid components). Thus, each cocoa butter nominally requires slightly different conditions to promote ideal solidification. Another source of differences in lipid crystallization among chocolates occurs when milk fat is used in the formulation since milk fat is widely known to inhibit cocoa butter crystallization. For these reasons, each chocolate requires slightly different tempering conditions to promote ideal solidification. The steps in chocolate solidification include nucleation, or seeding, to obtain the desired polymorph followed by cooling under appropriate conditions to allow the seeds formed in tempering to fully crystallize the rest of the cocoa butter as the chocolate solidifies.

As discussed in Chapter 4, lipids crystallize into different polymorphic forms depending on the nature of the fat and the crystallization conditions. Cocoa butter exhibits numerous polymorphs (Table 4.13), each with different stability, melting temperature, and physical attributes (e.g., volume contraction). Less stable polymorphs are most likely to crystallize first based on differences in crystallization rate, but these transform to more stable polymorphs at a rate that also depends on the nature of the fat (particularly the surface-active lipids that are present as impurities in cocoa butter) and the operating conditions. Formation of unstable polymorphs during chocolate solidification generally leads to bloom problems (see Section 15.9).

As covered in Section 15.5, tempering involves either adding the appropriate seeds to melted chocolate or somehow inducing nucleation of the cocoa butter to give the appropriate number, size and polymorphic form of seeds. Well-tempered chocolate is generally considered to contain somewhere between 1% and 3% cocoa butter seeds in the form of small, numerous crystals in the β V polymorphic form, although recent studies have shown that significantly less crystal seeds can still promote proper solidification of chocolate. Windhab (2009) claims that as low as 0.02–0.2% solid crystals are sufficient to seed chocolate with newer seed tempering methods.

Similar numbers were found by Kinta and Hartel (2010), who seeded chocolate with commercially available seeds (primarily β V cocoa butter polymorph) and found that only 0.137% seed material in the chocolate was sufficient to provide good solidification characteristics based primarily on surface appearance.

Even if a chocolate is well-tempered, it is well known that proper cooling conditions are mandatory to ensure high quality chocolate. For one, formation of unstable cocoa butter crystals occurs if the chocolate is cooled too rapidly, which can cause improper solidification. For example, if temperatures in the cooling tunnel are set too low, the liquid cocoa butter in tempered chocolate can nucleate into unstable polymorphic forms, despite the presence of a proper number of seed crystals. Thus, solidification of tempered chocolate must balance between nucleation of unstable polymorphs and the growth of existing seed crystals. Kinta and Hartel (2010) observed crystallization of cocoa butter with and without proper seed crystals by polarized light microscopy. Even when sufficient seed crystals for good temper were present (>0.137% seeds), unstable β′ polymorphic crystals nucleated quickly around the seeds. However, when sufficient seeds were present, they grew quickly enough to complete solidification of the cocoa butter before a sufficient number of unstable polymorphic crystals could form. When insufficient seeds were present, extensive nucleation of unstable polymorphs occurred, leading to bloom problems.

Tempering chocolate requires a detailed understanding of the chocolate itself since there are various formulation parameters that can affect cocoa butter crystallization and polymorphism. As noted previously, differences in molecular composition of one cocoa butter to another result in different crystallization and melting profiles. Typically, cocoa butters that are hard (higher level of saturates and monounsaturates) crystallize more readily than those that are softer (more polyunsaturated fats). That is, when cooled to the same temperature, harder cocoa butters crystallize more rapidly and to a higher solid fat content (SFC) than softer cocoa butters (Chaiseri and Dimick 1995a, b). In general, cocoa butters from Malaysia crystallize more rapidly than West African cocoa butters, which crystallize more rapidly than South American cocoa butters. Also, cocoa butters that contain certain types of phospholipids and other minor impurities, may crystallize more readily than a deodorized cocoa butter due to the nucleating capacity of the impurities (Davis and Dimick 1989). Even the polymorphic type of seed crystal can influence crystallization time, with the β VI polymorph being better at promoting crystallization than either the β′ or β V forms (Hachiya et al. 1989).

Other factors may slow crystallization and/or polymorphic transition. For example, addition of milk fat to chocolate causes a significant decrease in the rate of cocoa butter crystallization (Metin and Hartel 1998, 2012). Minor impurities (mono- and diglycerides, phospholipids, etc.) also typically slow the rate of polymorphic transformations (Garti and Yano 2001). Milk fat may also slow the polymorphic transitions of cocoa butter (Bricknell and Hartel 1998).

These differences in crystallization rate among cocoa butters due to differences in composition mean that, when exposed to the same time-temperature-shear (agitation) protocol during tempering, different chocolates will have different extents of seed crystal formation. Some chocolates may be over-tempered while other chocolates may be under-tempered. To account for this variability, tempering conditions are modified slightly to slow or speed crystallization and polymorphic transition to achieve the same level of temper (defined here as the proper number, size and polymorphic form of seed crystals). The operating parameters used to moderate crystallization during tempering include temperatures, heating and cooling rates, residence time at each temperature (and after tempering has been completed), and agitation/shear rate. In general, proper temperature-time-shear profiles must be found for each chocolate to attain the desired level of temper. Often, these conditions must be found empirically, by trial and error.

The first level of control for developing optimal temper in chocolate is the lowest point in the tempering process (see Figure 15.9). Lower temperatures increase the driving force for crystallization, promote more rapid nucleation and develop higher crystal seed content. Thus, cocoa butters that crystallize more slowly would be cooled to slightly lower temperatures in the initial stage of tempering to promote crystallization. Reducing tempering temperature to promote more rapid crystallization is used, for example, for milk chocolates to offset the inhibition of milk fat TAG on crystallization of cocoa butter. Milk chocolates are typically cooled to temperatures 1–2 °C (2–4 °F) lower than for dark chocolate to promote cocoa butter crystallization. Higher shear rates generally also promote nucleation of slow-crystallizing cocoa butters so use of a tempering unit that promotes shearing can also help offset slow cocoa butter crystallization. Slowly crystallizing chocolates might also be held longer at the lower temperature to allow more time for sufficient nucleation to be initiated.

Since crystallization at the low point in the tempering process promotes formation of unstable polymorphic forms (α and/or β′), the next step in tempering is to raise the temperature above the melting point of these unstable forms to cause them to melt away and transform to the stable β V polymorph. The temperature to which the chocolate is warmed determines how much of the cocoa butter remains in the crystalline state, whereas the number of crystals remaining is primarily set by the nucleation rate in the first stage of tempering and how many nuclei melt away. Again, differences in SFC of cocoa butters from different origins require different temperature profiles to ensure the right amount of seed crystals. If temperature is too high, there may potentially be too few crystals for adequate solidification. On the other hand, if temperature is too low, there will be too many seed crystals (higher SFC). The main problem in this case is most likely the increased viscosity that comes from having a higher SFC of the cocoa butter. To maintain consistent temper of chocolate, some trial and error is required to find the temperature where cocoa butter crystallization and the melting of cocoa butter crystal are in balance.

Once tempering is complete, the chocolate is ready for use. However, in commercial operations, there is usually a lag between when the chocolate has been optimally tempered and when it is actually used (deposited, enrobed, etc.). This can be problematic, especially if the time/temperature/shear scenario varies to any extent. The seed crystals present in tempered chocolate are not at a true equilibrium and are subject to change at a rate depending on holding conditions. For one, the seed crystals are not in their most stable polymorphic form and will slowly transform to the most stable β VI polymorph. In most cases, this is not an issue because the time scales for the β V to β VI transition are much longer than hold times in commercial operations. However, there are other thermodynamic effects that occur in fluid, but tempered, chocolate that lead to negative changes in degree of temper. A thermodynamic ripening phenomenon, Ostwald ripening, can occur when there is a distribution of crystal sizes. Smaller crystals (higher curvature) have a slightly lower melting point than larger, flatter crystals and under isothermal storage conditions, the small crystals can melt away at the expense of growth of larger ones. Typically, Ostwald ripening is most important for crystals less than a micron or two in size, which is the expected size of seed crystal in tempered chocolate. Although Ostwald ripening has not been documented to occur in tempered chocolate held at warm (30–32 °C) temperatures, the conditions are appropriate and it would explain the slow transformation of tempered chocolate into over-tempered chocolate. The difference in stability of crystals of different sizes is more of a concern under conditions where temperature cycles. Even temperature swings of 1 °C or so can be enough to cause melting of smaller, less stable, crystals and growth of larger crystals. Higher temperature cycles promote this ripening process and hasten the development of over-tempered chocolate. In chocolate processing, tempered chocolate should be used as quickly as possible to minimize these changes and any temperature fluctuations should be minimized as well. If tempered chocolate is held too long so that it becomes over-tempered, it can simply be re-melted and re-tempered for continued use. Some tempering units in enrobers, for example, utilize a re-heating cycle to ensure an adequate supply of tempered chocolate even over long periods of use.

15.9 Chocolate Stability and Shelf Life

Standard storage conditions for chocolate are 20 °C (68 ° F) ± 1.5 °C with a relative humidity of 40–50%. Storage areas should have consistent temperatures throughout and be free of off odors. Freshly tempered chocolate items should be fully solidified before being placed in cold storage. This will prevent the possibility of unstable fat phase change, which can lead to premature fat bloom. Well-tempered chocolate stored at proper conditions has a shelf life of at least 1 year (white chocolate) and up to 2 years (dark chocolate) depending on formulation. When stored for longer than a year even at ideal conditions, subtle changes take place in the chocolate that lead to decreased quality. These include flavor loss, increased viscosity of the melted chocolate, and gradual surface dulling over time. Chocolate is microbiologically stable because of its low water activity. Several factors can reduce shelf life if storage conditions are not ideal. Primarily, the end of shelf life of chocolate is caused by sugar bloom, fat bloom or the pick-up of moisture or off flavors. Martin (2000) provides a detailed description of factors that influence shelf life of chocolate confections.

15.9.1 Sugar Bloom

Sugar bloom (less common than fat bloom) and fat bloom look somewhat similar in that there is a white film on the outer surface of the chocolate. The white film on chocolate that is sugar bloomed is crystalline sugar from when it was exposed to water. A water drop on a chocolate surface, whether from vapor condensing on a cold chocolate surface or drops of water contacting the chocolate, dissolves sugar crystals near the surface. Some of the water actually penetrates slightly into the chocolate, dissolving sugar crystals as it goes. Through interfacial forces and the approach to equilibrium (saturation of the water with sugar) within the water phase, the water droplet at the surface seems to “draw” sugar out of the chocolate until, given enough time, the sugar concentration in the water droplet reaches the solubility concentration at the storage temperature.

When the water later evaporates from that droplet on the chocolate surface (for example, when the chocolate is exposed to dry air), the sugar solution remaining in the droplet becomes increasingly supersaturated and eventually crystallizes. As water continues to evaporate, eventually all of the sugar recrystallizes on the surface of the chocolate when the droplet dries out. Once recrystallization occurs, the sugar remains at the surface and does not return to the interior of the chocolate from which it initially came. The resulting white film of white sugar crystals at the chocolate surface gives an uneven appearance, perhaps even looking like mold to the consumer.

A simple method to distinguish sugar bloom from fat bloom is to place a warm dry finger on the bloomed surface. Sugar bloom does not disappear over time from the warmth of the finger, whereas fat bloom will shrink as the warmer temperatures melt away some of the fat. An alternative method for determining sugar bloom is to place a drop of water on the surface of the chocolate. If the drop of water spreads out, it is sugar bloom. If it remains beaded as a drop of water, this indicates fat bloom. Once sugar bloom has occurred, there is little hope of reclaiming the glossy surface of well-tempered chocolate.

The best solution to sugar bloom is to avoid water and humidity conditions that could lead to condensation. For example, cooling tunnel temperatures are set so that the chocolate temperature upon exiting the tunnel is above the dew point of the environmental air. Should the chocolate temperature fall below the dew point, the cold chocolate surface provides an excellent spot for water vapor to condense from the air, leading eventually to sugar bloom. Cooling tunnels should also be checked for high relative humidity conditions or accumulation of condensate.

A similar problem of sugar bloom may occur if chocolate is refrigerated or frozen. Storage at such low temperatures is actually good for extending the shelf life of the chocolate and most chocolate coated confections; however, the potential for sugar bloom is high unless precautions are taken to prevent the cold chocolate surface from coming into direct contact with humid air. Specifically, chocolate intended for refrigeration or freezing should be well wrapped and the package completely sealed to avoid moisture penetration. When the chocolate is removed from the cold environment, it should be allowed to warm up gradually to room temperature before the package is removed. A typical scenario is to move chocolate items from freezer to refrigerated conditions to ambient temperature in stages.

15.9.2 Bloom on Untempered Chocolate

The main purpose of tempering is to precrystallize the cocoa butter so that upon cooling and forming, the remaining liquid cocoa butter crystallizes into the proper polymorphic form. If chocolate is not tempered, it quickly forms a unique type of bloom on the surface of the chocolate and a crumbly interior texture.

When untempered chocolate is cooled, a surface haze forms on the chocolate, often within the first few hours of solidification, although sometimes it takes a few days for surface structures to appear, as seen in the example shown in Figure 15.23. These surface structures continue to develop over a period of days. The appearance of bloom on untempered chocolate is different from other types of bloom in that it typically appears as dark brown spots, mostly circular, amidst a sandy white background (Figure 15.23). From careful analytical work (Kinta and Hatta 2005; Lonchampt and Hartel 2006; Kinta and Hartel 2010), it has been shown that these sandy white areas are actually depleted in fat, suggesting that these regions have become concentrated in sugar crystals and cocoa solids (and milk solids for milk chocolate).

The phase separation between cocoa butter and the particulates in chocolate occurs because of the polymorphic nature of cocoa butter. When untempered chocolate is cooled, the cocoa butter must nucleate by itself (as opposed to tempered chocolate, where cocoa butter seed crystals present from tempering simply have to grow). At the cooling conditions typical of cooling tunnels, cocoa butter crystallization is relatively slow, particularly because there is no agitation to promote nucleation. Thus, only relatively few nuclei form and these are in the α and/or β′ polymorph. These unstable polymorphs transform over time into the stable β V and β VI forms. In doing so, there is a release of latent heat and further contraction of the stable polymorphic crystals. These forces are sufficient to separate fat from particulate matter, leaving the mounds of sucrose crystals and cocoa solids to mar the surface appearance.

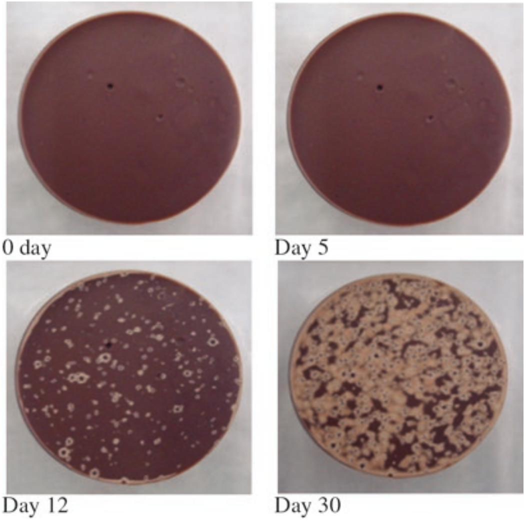

Figure 15.23 Surface appearance of bloom on untempered chocolate

15.9.3 Bloom on Undertempered Chocolate

In undertempered chocolate, there are insufficient seed crystals to dominate cocoa butter crystallization upon cooling so that uncontrolled nucleation of unstable polymorphs dominates. As in untempered chocolate, the conversion of unstable to stable polymorphs causes shifts and changes in the particle structure, eventually leading to appearance of surface irregularities (Kinta and Hartel 2010).

Afoakwa et al. (2009b) studied the changing appearance of under-tempered chocolates made with different particle sizes. Using stereoscopic binocular microscopy, they followed changes of the surface structure as under-tempered chocolate solidified and developed bloom over time. They found evidence for liquid fat appearing at the surface followed by formation of regions of recrystallized fat. This occurred more rapidly when particle (sugar, cocoa solids) size was largest (≈50 μm) and more slowly as average particle size decreased, suggesting capillary forces influence liquid fat migration. The lipid recrystallization at the surface eventually led to separation of the particulate phase at the surface, giving the well-known sandy surface characteristic of untempered and, to some extent, undertempered chocolate.

15.9.4 Storage Bloom on Tempered Chocolate

Much has been written about the type of bloom that occurs during storage of well-tempered chocolate (Timms 2003; Lonchampt and Hartel 2004; Widlak and Hartel 2012; etc.). Jewell (1972) showed that fat bloom during storage is due to the appearance of large fat crystals (2–10 μm long by 0.5–2 μm wide by 10–50 nm thick) emanating from the surface of the chocolate, although similar crystal formation is often found within the bulk of the chocolate as well. Fat bloom occurs gradually during storage at a rate dependent on the conditions. Despite the numerous studies on the topic, our understanding of the exact mechanisms that lead to bloom is still unclear. In part, this is because there are myriad factors that can influence storage bloom, including a range of formulation factors and storage conditions.

Formulation factors that can influence bloom formation include the nature and origin of the cocoa butter as well as phase mixing effects with other fats. Even though all cocoa butters have much the same molecular composition, it seems that some chocolates are more prone to bloom than others. Little has been written about this, but differences in bloom propensity between chocolates must be related to the specific composition of the TAG and other minor components. Previous studies have noted that addition of certain TAG normally found in cocoa butter, specifically SOS and POP as well as the asymmetrical TAG SSO or PPO, can inhibit bloom by inhibiting the polymorphic transformation to the β VI form (Padley et al. 1972; Arishma and McBrayer 2002). It could be that cocoa butters with naturally higher levels of these TAG are more resistant to bloom because they crystallize more readily and form a tighter cocoa butter crystal network that is resistant to liquid oil migration. The natural surface-active components (emulsifiers) found in cocoa butter may also provide a measure of bloom inhibition, since certain emulsifiers can potentially have a strong effect on bloom in chocolates (Easton et al. 1952).

In some cases, mixtures of different cocoa butters are used in a chocolate, and these mixtures may be less stable than either of the original cocoa butters. Again, this must be related to the range of chemical constituents in each cocoa butter. Other mixtures of fats in the chocolate (i.e., milk fat, other vegetable fats where allowed) may result in phase separation and recrystallization on the surface or even within the bulk of the chocolate. However, sometimes these mixtures can provide an element of bloom inhibition, as found with addition of milk fat. Migration of another fat into the chocolate from a center (e.g., nut oil) or a cookie (e.g., shortening) can also lead to bloom, but this type of bloom will be treated separately in the next section.

Improper storage conditions can also enhance the rate of bloom formation over time, although even under the most ideal storage conditions (cool temperatures, low humidity), most chocolate will eventually bloom. In particular, temperature cycling generally leads to more rapid bloom formation, particularly when combined with elevated temperatures between room temperature and the melting point of cocoa butter. Of course, if temperature exceeds the melting point for a sufficient amount of time to melt all of the cocoa butter crystals, then upon recooling, untempered fat bloom will most likely occur.

Numerous mechanisms appear to influence bloom on chocolate during storage, but in general they all come back to the polymorphic transition of cocoa butter to its most stable form, the β VI polymorph. It is widely thought that bloom in fact is caused by this polymorphic transition, but that is not the case. Several studies (Bricknell and Hartel 1998; Adenier et al. 1993) have clearly shown that the presence of the β VI polymorph does not always lead to visual bloom. These studies have proven that, under the right circumstances, the polymorphic transition can occur at the surface of the chocolate without development of the white surface haze associated with visual bloom formation. However, in all cases when bloom has been observed on chocolate, the most stable cocoa butter crystal form, the β VI polymorph, has also been observed. Thus, it seems that the polymorphic transition is a necessary step in bloom formation, but by itself, the polymorphic transformation is not sufficient to always lead to bloom formation. For the appearance of visual bloom on chocolate, the recrystallized cocoa butter crystals must also grow in such a way that they appear as spikes or needles emanating from the surface (Figure 15.24).

The specific mechanisms responsible for this surface bloom are complex, depending on the composition and storage conditions. In brief, storage bloom (not due to lipid migration from a nut or biscuit center) is thought to take place in several steps (Hartel et al. 2016). First, liquid phase of cocoa butter (cocoa butter is about 15–25% liquid at room temperature) within the chocolate migrates towards the surface of the piece, due either to capillary forces or a pumping action related to temperature fluctuations. The occurrence of liquid fat at the surface of chocolate during bloom formation is suspected but not verified. Dahlenberg et al. (2011) observed what they thought to be liquid fat at the surface of under-tempered chocolate, which recrystallized over time. Evidence by Hodge and Rousseau (2002), using atomic force microscopy to probe surface characteristics, also suggests liquid-like cocoa butter, often in the form of cones, appearing at the surface of chocolate. These cones then were seen to recrystallize in a form resembling the spiky crystals typically seen emanating from the surface as bloom. Both Smith and Dahlman (2005) and Hodge and Rousseau (2002) also note the rough surface characteristics at a scale of a few microns, with numerous cracks and crevices (pores or holes) that could supposedly be conduits for liquid fat migration. However, Rousseau (2006) suggests that there are no changes in the pores themselves and downplays their potential role in liquid fat migration and bloom formation.

Regardless of the role of these pores, or cracks and crevices, as conduits for liquid fat, the particulate structure can influence oil migration within the chocolate (Hartel et al. 2016). A matrix with a high particulate phase volume comprised of numerous small particles provides a difficult matrix for liquid oil migration (Ghosh et al. 2004). Thus, chocolate that is made up of particles (sugar crystals, cocoa solids, milk powder, etc.) that pack tightly together along with the tightest cocoa butter crystal structure would provide the most resistance to liquid oil migration (most tortuous path) and should provide the maximum resistance to storage bloom. The surface characteristics and shape of the particles may also play a role in determining the ability of liquid oil to migrate through the chocolate.

Once liquid fat migrates to the surface, recrystallization of the cocoa butter must occur. However, liquid fat that has migrated to the surface will not recrystallize (it is liquid because its melting point is low), but this liquid fat dissolves a small portion of the high melting components of cocoa butter (Adenier et al. 1993; Timms 2003; Zhou and Hartel 2006), as shown previously in Figure 4.10. Even though the solubility of high-melting fat in liquid oil is low (<1%), that small amount is sufficient to cause recrystallization at the surface, particularly when temperature fluctuations cause the temperature to decrease below the solubility level. Recrystallization of the cocoa butter at the surface occurs primarily on rough edges, cracks and crevices. These rough surfaces promote growth of crystals of the most stable polymorph of cocoa butter, with the crystals forming spikes or needles that grow out of the surface. This causes diffuse reflection of light, which appears as a dull and whitish surface. A rough surface containing jagged sugar crystal fragments appears to be necessary for this recrystallization process since a chocolate made with

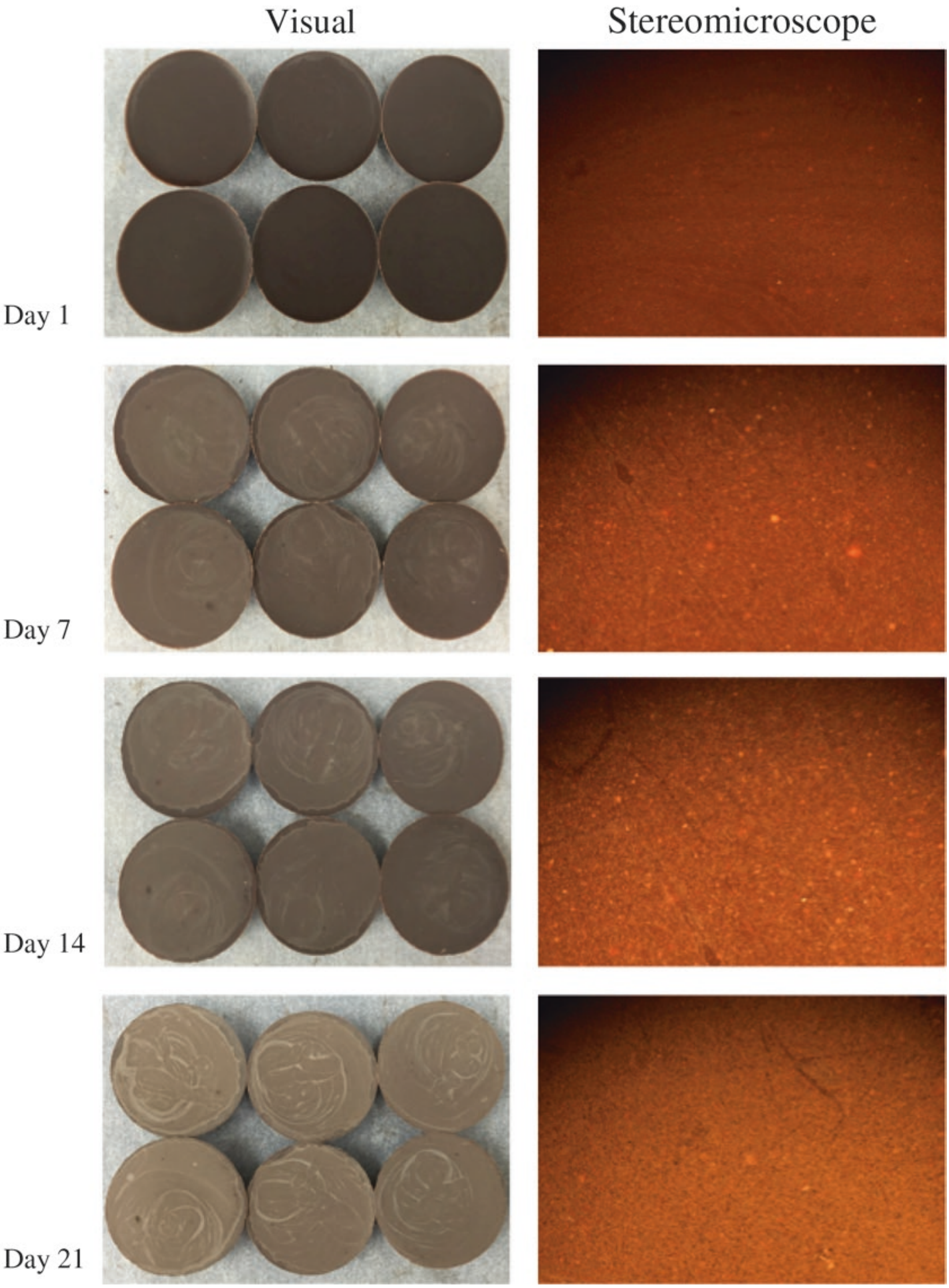

Figure 15.24 Surface appearance of bloom during storage of tempered chocolate

smooth-surfaced, spray-dried sugar particles did not form bloom despite confirmation of the polymorphic transformation from β V to β VI (Bricknell and Hartel 1998). Or perhaps the rounded particles in this study influenced the liquid fat migration to the surface. A similar mechanism for bloom formation involving recrystallization of a high-melting fat dissolved in a liquid oil has been hypothesized for bloom formation on lipstick and similar cosmetics, where recrystallization of stearic acid occurs on the surface of a wax/oil/particle matrix (Matsuda et al. 2001).

When recrystallization of the cocoa butter occurs at the surface, the more stable polymorph (β VI) forms. In part, this polymorphic transformation is thermodynamically driven, but it must also be in part because crystallization occurs from the liquid oil solvent (the β VI form typically does not crystallize by itself unless dissolved in a solvent). Although the exact nature of this recrystallization step is not yet completely understood, Peschar et al. (2004) consider the molecular orientation of specific TAG in cocoa butter to play a major role. Their work with synchrotron x-ray powder diffraction shows that the oleic acid moiety of SOS, which most closely describes the crystal lattice of cocoa butter, allows room for rearrangement into the more stable β VI polymorph.

There is also most likely a slight molecular purification during this recrystallization, where some of the lower melting point TAGs are excluded from the crystal lattice during nucleation and growth. Some studies have suggested there is a slight increase in oleic and palmitic acids and a slight decrease in stearic acid in bloom crystals. However, literature studies that have characterized the chemical composition of bloom compared to the underlying chocolate are often contradictory and only show relatively small effects (Lonchampt and Hartel 2004).

Although the above steps are most likely the primary cause of bloom during storage of chocolate, there may be conditions where the phase behavior of the molecular constituents of cocoa butter undergo a thermodynamic phase separation. Cocoa butter crystals are predominantly co-crystallized SOS, POP and POS molecules, which can undergo phase separation under the right conditions (Loisel et al. 1998).

15.9.4.1 Minimizing Storage Bloom

Numerous approaches have been explored for inhibiting bloom formation during storage. These include both formulation factors (including addition of specific bloom inhibitors), processing factors and storage conditions.

A high quality cocoa butter with good inherent bloom stability should be used. TAG composition and/or minor components (phospholipids, mono- and diglycerides, etc.) present in the cocoa butter can influence crystallization rate and thus, the nature of the cocoa butter crystals (size, distribution, network formation, etc.) in the solidified chocolate. In general, a tightly packed network of small cocoa butter crystals minimizes liquid oil migration in the chocolate and retards bloom formation. Ideal tempering conditions will also ensure the most effective crystalline network for bloom inhibition.

There is good evidence that the nature of the particulate phase in chocolate can influence bloom formation (Afoakwa et al. 2008b; Jin and Hartel 2015; Hartel et al. 2016). Both the cocoa butter crystal network and the dispersed particulates contribute to the tortuosity of the matrix to liquid cocoa butter migration. To reduce liquid fat migration and inhibit bloom formation, methods of enhancing the tortuosity should be explored. Specific particle size distributions may inhibit the ability of liquid cocoa butter from migrating through the solid matrix. For example, the proper mixture of smaller particles that can fill the interstitial spaces between larger crystals could enhance the tortuosity of the matrix and retard oil migration. One simple approach to increase the tortuosity of the chocolate matrix is to lower temperature, causing more of the cocoa butter to be in the crystalline state. The denser cocoa butter crystal network and the reduction in the amount of liquid oil both contribute to reduced oil migration and better bloom stability.

Various bloom inhibitors have been developed over the years for addition to chocolate although their use is often restricted by regulations related to the Standard of Identity. One bloom inhibitor allowed worldwide is milk fat. Milk fat, particularly the high-melting components, is known to be a highly effective bloom inhibitor (Bricknell and Hartel 1998). As such, milk chocolate is highly resistant to bloom and even small amounts of milk fat in dark chocolate can be effective in inhibition of storage bloom. In particular, the high-melting components of milk fat have been found to greatly reduce bloom during storage of chocolate (Lohman and Hartel 1994). In the same study, the lowest melting components of milk fat were actually found to enhance bloom formation, perhaps by increasing the amount of liquid fat present in the chocolate. It has been shown that the high-melting fraction slows the polymorphic transition from β V to β VI (Bricknell and Hartel 1998).

As noted earlier, certain TAG normally found in cocoa butter can provide bloom stability when added to chocolate. These include SOS, POP, SSO or PPO (Padley et al. 1972; Arishma and McBrayer 2002). Other TAG can also provide a measure of bloom protection. For example, Talbot (1994) described a commercial product with tailored TAG that was found to provide enhanced bloom stability. The exact mechanism by which these TAG inhibit bloom is still uncertain, although in general they are thought to slow the polymorphic transition from β V to β VI.

It has been known for a long time (Easton et al. 1952) that emulsifiers can have a strong effect on bloom during storage. For example, DuRoss and Knightly (1965) showed that sorbitan monostearate (SMS) and polysorbate 60 provide a distinct advantage in reducing the rate of bloom formation during storage. These effects may be due either to enhancing crystallization of cocoa butter to create a denser cocoa butter crystal network to limit fat migration or, more likely, to an inhibition of the polymorphic transition from β V to β VI (Lonchampt and Hartel 2004).

Finally, storage conditions should be controlled to minimize the factors that promote liquid oil migration and recrystallization. Specifically, cool temperatures and minimal temperature fluctuations provide the longest shelf life for chocolate. Low temperature storage provides high solid fat content (low liquid oil content), thereby reducing liquid oil migration. The rate of polymorphic transition is reduced at low temperatures as well. Storage with temperature fluctuations is generally regarded as being deleterious for good shelf life. In fact, temperature fluctuations are often used to accelerate bloom studies (Lohman and Hartel 1994; Jin and Hartel 2015). High temperatures during thermal fluctuations cause melting of cocoa butter crystals, leading to greater liquid fat and a less tortuous matrix. This promotes liquid fat migration, but the main problem comes when temperature decreases again. The liquid fat that has migrated to the surface is now exposed to colder temperatures where the solubility of the high-melting components in the liquid oil is lower. This means a larger amount of high-melting fat crystallizes out, giving rise to enhanced bloom. The higher temperatures also promote faster polymorphic transition from β V to β VI. Another potential mechanism for enhanced bloom at cycling temperatures relates to changes caused by Ostwald ripening of the cocoa butter crystal network. Smaller crystals tend to disappear and larger crystals grow, leading to a more open matrix (less tortuosity) that allows easier liquid fat migration.

15.9.5 Lipid Migration and Fat Bloom

In multi-domain chocolate products (i.e., chocolate and nuts, chocolate-covered biscuits, etc.), migration of oil or shortening from the nuts or biscuit is known to lead to fat bloom (Ghosh et al. 2004). Lipid migration occurs in these products due to the differences in concentration of individual triacylglycerols (TAG) in the two regions. For example, nut oil is high in polyunsaturated fats, whereas cocoa butter is high in specific monounsaturated TAG (SOS, POP, POS). This difference in composition is thermodynamically unfavorable and TAG diffuse from one region to the other in an attempt to come to thermodynamic equilibrium.

As a more liquid fat (e.g., nut oil) migrates into chocolate, there is a continual change in the phase behavior of the new mixed system. Since nut oils cause dilutional softening of cocoa butter, some of the crystalline cocoa butter must dissolve in the liquid oil to maintain phase equilibrium. In principle, the amount of cocoa butter crystals that dissolve is directly proportional to the amount of nut oil that penetrates the chocolate. In a real sense, the nut oil solubilizes the higher-melting cocoa butter TAG, forming a solution system. This decrease in crystalline cocoa butter in the chocolate (and increase in liquid nut oil) causes the chocolate to soften considerably. It is also more prone to bloom formation since there is more liquid fat to migrate through the chocolate and to the surface, where eventually the higher-melting cocoa butter TAG recrystallize to form bloom spots.

To reduce bloom due to lipid migration, either the driving force for diffusion must be reduced or the rate of diffusion must be constrained. Changing the driving force is not possible since that would require changing the composition of the two fats. Thus, changing the rate of diffusion of the oil TAG into the chocolate is the best option. First, making sure the chocolate is well-tempered, with the densest network of small cocoa butter crystals. This will minimize the rate of the nut oil TAG diffusion and reduces the rate of bloom formation due to lipid migration. Second, reducing the rate of diffusion of oil out of the center can also delay problems associated with lipid migration. Changing the nature of the matrix through incorporation of hard crystalline fat might slow nut oil migration in the same way a stabilizer is used to prevent oil separation such as in peanut butter. The use of whole nuts rather than chopped nuts will provide less free fat for lipid migration as does the use of dry roasted nuts rather than oil roasted nuts. Also, decreasing temperature of storage can reduce diffusion rates. Finally, a barrier layer between the center or cookie and the chocolate coating layer can effectively reduce the rate of migration between the two components. Potential oil barriers might include a thin layer of maltodextrins, gums and/or waxes. Pre-coating of nuts prior to panning is an example where this practice is used. Although the potential of edible barriers is enormous for limiting oil migration, the practical aspects of forming a complete layer, without open channels, over the entire contact surface area has been difficult to realize. Furthermore, many types of barriers impart negative sensory attributes to the product.

15.9.6 Off Flavors

Chocolate during storage is susceptible to sorption of off-flavors and odors that can ruin the delicate flavor profile of chocolate. It should be kept tightly packaged and kept away from other materials (spices, mint flavors, cleaning supplies, etc.) and processes (painting, engine fumes, floor sealing, etc.) from which it can pick up off flavors. Chocolate stored in a refrigerated or freezer areas must also be properly packaged to prevent pick up of undesirable odors. Typical packaging materials used for chocolate products, such as biaxially oriented polypropylene (OPP), are resistant to vapor/gas transport and provide decent protection against flavor uptake (Martin 2000).

15.9.7 Oxidative Deterioration

Chocolate is typically quite resistant to oxidative deterioration. Although oxygen is not excluded in chocolate packaging, the inherent nature of chocolate makes it quite resistant to lipid oxidation. Cocoa butter contains a relatively low level of polyunsaturated fats, providing enhanced stability against oxidation. In addition, cocoa solids also contain natural antioxidants (e.g., tocopherol) that provide a measure of protection against oxidation. White chocolate, which contains no cocoa solids and often uses deodorized cocoa butter that has few natural antioxidants, is much more prone to oxidation (particularly light-induced oxidation) than regular chocolate. For this reason, antioxidants are allowed in the formulation of white chocolate.

In general, the changes that occur in milk fat (oxidation) and in the cocoa butter (polymorphic transformation) lead to a gradual stale flavor development in white chocolate with a reduced flavor release. For this reason, the typical shelf life of white chocolate is about 12 months, primarily due to the high milk fat content. Due to the increased levels of natural antioxidants, milk chocolate will have a nominal shelf life of 18 months while dark chocolate is suitable for consumption up to 24 months with proper storage and packaging.

15.10 Rework of Chocolate and Chocolate Confections

As with any manufacturing process, there will be in-process and finished products that do not meet quality standards. These unacceptable products are often called rework or scrap. It is in the best economic and environmental interest of the manufacturer to minimize any rework that is produced. Rework can be part of the ongoing production process such as scrapings, trimmings, doubles, and broken pieces or the occasional misfortune such as an entire lot of underweight or poorly tempered product. All causes of rework need to be reviewed so that the total amount produced is minimized or eliminated.

15.10.1 Reworking Chocolate

Plain chocolate that needs to be reworked is much easier than chocolate confections. Candidates for chocolate rework include items that are improperly tempered, decorated, visually not acceptable (bloomed, broken bars, scuffed, poor demolding, etc.) or part of the process such as the beginning or end of an operation or when switching to a different chocolate type.

The first consideration of reworking any product is hygienic. It must be handled like any other food ingredient to prevent any microbiological or inclusion issues. The best case scenario is to rework ‘like into like’. This will simplify lot tracking, labeling and allergen concerns. The wonderful thing about chocolate is that it can be retempered as many times as necessary to produce a beautiful finished product. Broken bars or those with poor temper can be melted and retempered to re-enter the product stream. All tempered chocolate should be screened to remove any potential inclusions.

Ideally only one chocolate type is ever used on a particular product line or it is allergen cleaned when different chocolate types are used. Since this is not always possible, the amount of chocolate that has to be reworked can be minimized by having chocolate lines that are sloped, self-draining and can be ‘pigged’ or air blown. New equipment designs, such as enrobers with removable troughs for cleaning or a separate trough used to maintain a chocolate identity, can also minimize chocolate rework.

The order in which chocolate items are produced can also affect the amount of chocolate rework. Generally, going from producing white chocolate items to milk to dark will minimize unacceptable product due to product changes. Label and allergen declarations must also be considered before these procedures are implemented.

Finally, any chocolate rework that has seized due to excessive heat or the addition of water can seldom be reclaimed. If the flavor is acceptable and if seizure of the chocolate is due to the addition of potable moisture, the addition of an emulsifier such as lecithin or cocoa butter may be a solution.

15.10.2 Reworking Chocolate Confections

Chocolate confections rework that contain inclusions and ingredients in addition to chocolate can be challenging and can come from many sources. Enrobed items that are underweight, scuffed or have poor gloss and temper can be reworked by simply re-enrobing the confections with a low viscosity chocolate.

Chocolate items that have a firm low moisture inclusion (such as chocolate nut clusters) can be melted and sieved to remove any inclusions. Often, cocoa butter is added to the melted mass to reduce viscosity and reclaim more of the chocolate. The reclaimed chocolate needs to be evaluated for particulate matter, fineness, viscosity, flavor, microbiological, and allergen/labeling concerns.

Chocolate items that contain a high moisture center such as caramel, fudge, truffles or creams can usually not be reworked as chocolate. However, these confections can be used as part of the existing center or as a new product center. These reworked items should be considered as an ingredient in making a center mass. As an example, chocolate covered caramel can be melted and brought to the same moisture as the existing caramel premix before cooking. When the rework is used at the same rate as being produced, the formula can be rebalanced for sugars and fats and used as part of the new ongoing caramel formula.

All rework should be considered as a food ingredient and be properly labeled and stored. Rework should be used as soon as possible and never exceed more than one fourth of its finished product shelf life. The greatest economic loss is when rework is used as animal feed, fat reclamation or waste disposal. The appropriate regulations should be reviewed to see which options are viable.

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Compound Coatings

16

16.1 Introduction

It might seem that a material that looks like chocolate, smells like chocolate, and tastes like chocolate, must indeed be chocolate. Not necessarily, if it is a compound coating. Loosely, a compound coating is any material that looks, smells and even tastes like chocolate but that, for one reason or another, does not meet the legal requirements (Standard of Identity) of chocolate and so, cannot be called chocolate. That is, a compound coating contains an ingredient (or ingredients) not specified in the Standard of Identity (see Section 15.1) or a permitted ingredient not at the right proportion to fit within the Standard of Identity. For example, the fat phase may be a different fat than cocoa butter, a nonnutritive sweetener may be used in the coating or the coating may contain flavors not specified for chocolate.

Historically, compound or confectioners coatings came into their own during the 1950s due to a sudden spike in cocoa prices (Urbanski 2009). When the price of cocoa increased substantially, manufacturers sought options to reduce the cost of making chocolate coatings. Replacing the cocoa butter was the primary alternative since it is the highest cost ingredient in chocolate. However, at that time, very few alternatives to cocoa butter were available from fats and oils suppliers, especially with the same desirable melting properties of cocoa butter (see Section 15.8.4). At that time, hydrogenation was the primary method for treating natural fats to modify melting profiles and only a limited number of products were available. In general, compound coatings or imitation chocolates, developed a reputation of being a cheap alternative to chocolate because the fat phase did not mimic very well the melting profile of cocoa butter. Advances in fat modification technologies over the past five to six decades have vastly improved the options available for coating manufacturers so that coating quality can now rival that of chocolate.

Many names exist for chocolate-like materials that do not meet the Standard of Identity for chocolate. Products may be called “chocolate-flavored”, “chocolatey” or even “fudgey”, but they cannot be called by the standardized terms for chocolate defined in the Code of Federal Regulations. Regardless of what they are called, compound coatings play an important role in the food (and confectionery) industry. Compound coatings are typically used in the same way as chocolate. They can be molded, enrobed, and panned. They can be used for candy fillings, exterior decorations, and as inclusions in other products (e.g., cookies and bars). Because the ingredients can be tailored to meet the specifications of the application, compound coatings often give food manufacturers added flexibility or allow them to do things not allowed under the chocolate Standard of Identity. For example, pastel coatings, which come in a variety of colors and flavors, provide unique benefits in numerous food applications. Yogurt-

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flavored compound coatings are common for panned goods and enrobed bars. Compound coatings containing fats with high melting point can be used to provide enhanced moisture and lipid barrier properties as well as in melt-resistant applications. And, in general, compound coatings can be produced for significantly less cost than chocolate, so provide significant cost savings.

Compound coatings generally have the same desirable properties as chocolate. That is, they should have a shiny surface appearance and dry touch (at room temperature). As far as possible, compound coatings should have similar texture and melting properties as chocolate. They should be easily processed to help reduce costs. Similar melting properties and flavor release during consumption are desirable. Finally, compound coatings should have a long shelf life, at least as long as chocolate. For the compound coating manufacturer, maintaining these properties at a reduced cost can be a significant challenge.

16.2 Formulations and Ingredients

Unlike chocolate, compound coatings can have nearly unlimited composition, as long as the finished product retains the desirable qualities as outlined in the previous section. For the most part, compound coatings are made with nearly the same ingredients as chocolate, with several major exceptions. First, the fat phase in compound coatings can be derived, in part or in full, from any fat that meets the requirements of the application. Second, different sweeteners can be employed to meet any need; for example, sugar-free coatings can be made with maltitol in place of sugar. Third, compound coatings can come in a variety of flavors and colors, whereas chocolate can have no added color and is limited in what ingredients and flavors can be added.

16.2.1 Ingredients

The properties of compound coatings are governed primarily by the same parameters that govern the properties of chocolates. Specifically, it must look and taste like chocolate as well as have the same physical attributes (melting profile, snap, etc.). Thus, the coating manufacturer must carefully choose fat, sweetener, emulsifier and flavors to suit the specific applications.

16.2.1.1 Fat

The primary difference between most compound coatings and chocolate is the source of the fat phase. In chocolate, only cocoa butter and milk fat (at some level) can be used according the US Code of Federal Regulations. Although some countries allow up to 5% of certain vegetable fats within the standards for chocolate, no such limitation on the type of fat applies for compound coatings.

In fact, any fat can be used as long as it meets the specifications (melting profile, etc.) of the application. In reality, commercial constraints often govern which fats are viable, as for example seen with the recent move away from fats that contain *trans* fatty acids. Historically, confectionery fats have been categorized as either lauric or nonlauric fats, based on the primary fatty acid composition. Lauric fats are those that contain a significant portion of lauric acid (C12:0), whereas nonlauric fats typically contain longer-chain fatty acids like palmitic (C16:0), stearic (C18:0) and oleic (C18:1) in addition to some polyunsaturated fats (see Table 4.1). Palm kernel and coconut oils are the primary lauric fats used in the confectionery industry, with palm kernel oil finding the majority of application in compound coatings. Palm, shea nut, cottonseed, soybean, canola, sunflower, safflower and peanut oil are all nonlauric fats that can be used in compound coatings, although most require substantial modification to achieve the functional properties needed. Lauric and nonlauric fats have different compatibility with cocoa butter, itself a nonlauric fat, and this level of compatibility often determines their use in coatings. This compatibility is related to the interactions among the specific triacylglycerols (TAG) present in each fat (see Section 4.3.2.3).

Based on their compatibility with cocoa butter, fats used in compound coating are typically characterized as either cocoa butter equivalents, replacers or substitutes (Lipp and Anklam 1998; Timms 2003). Lipp and Anklam (1998) provide detailed composition data for cocoa butter and a variety of cocoa butter alternative fats.

16.2.1.1.1 Cocoa Butter Equivalent (CBE)

CBEs are chemically (TAG, etc.) and physically (melting point, etc.) equivalent to cocoa butter. Because of this, CBEs can be added at any level to cocoa butter since they are completely compatible. That is, they contain the same types of TAG: SOS, POP and POS (P-palmitic; S-stearic; O-oleic). Tropical fats, such as palm, shea, ilipé, kokum, sal and mango, fit into this category. Although these fats do not have the exact same TAG composition as cocoa butter, combinations of fractions from these sources can be made that closely mimic cocoa butter.

CBEs are often further distinguished as cocoa butter extenders (CBEx) and cocoa butter improvers (CBI). CBEx may not be compatible at all mixture levels whereas CBI usually have more high-melting TAG to help improve characteristics of soft cocoa butters.

Traditionally, CBEs have been used in chocolates, where allowed, at relatively low levels to enhance the properties of cocoa butter. In many countries, up to 5% of certain CBEs are allowed within the standard definition of chocolate. More recently, however, compound coatings with increased levels of CBE in various mixtures with cocoa butter have become common. For example, “super” compounds are now available, where all the extra fat added, over and above the cocoa butter in the chocolate mass, is comprised of a CBE. Because the melting properties of the CBE closely mimic those of cocoa butter, super compounds closely mimic real chocolate (all cocoa butter), but with certain advantages. The CBE can be tailored to the application (e.g., melting point) and are said to provide enhanced bloom stability, faster processing (crystallization) time, and cost savings. They may also be less susceptible to softening by milk fat in milk chocolate coatings. However, because they behave essentially like cocoa butter, CBE must be tempered in the same way as cocoa butter to develop a stable polymorphic crystal form.

16.2.1.2 Cocoa Butter Replacers (CBR)

Fats that replace a portion of the cocoa butter in a coating formulation are considered as CBR. These are typically fats with similar fatty acid chain length (C16:0, C18:0 and C18:1) as cocoa butter, but with different arrangement of the fatty acids on the TAG. For this reason, they are typically only compatible with cocoa butter up to a certain level, about 20%. Higher levels generally lead to excessive softening and bloom problems. CBR are nonlauric fats usually made through modification of palm, soybean or cottonseed oils.

In the past, these vegetable fats have been partially hydrogenated to raise the melting point to more closely mimic the melting behavior of cocoa butter. However, since formation of elaidic acid (C18:1 *trans*) commonly occurs during hydrogenation, partially hydrogenated vegetables fats used for nonlauric-coatings typically contained well over 40–50% *trans* fatty acids; it is this problem that has seen their use decline precipitously over the past decade or two. In fact, partially hydrogenated fats no longer have GRAS (generally recognized as safe) status, so they are no longer in use.

Alternatives to hydrogenated CBR are available based on mixtures of palm oil fractions, but these CBR fats often have other issues (e.g., slow crystallization) that limit their application. They are typically used for soft applications and fillings.

16.2.1.3 Cocoa Butter Substitutes (CBS)

Lauric fats, when hardened appropriately, find favorable application as a substitute for cocoa butter in compound coating recipes, generally as a substitute for all of the cocoa butter in the coating formulation. Typically, palm kernel oil is the most common lauric-based coating fat, modified in such a way as to better mimic the melting properties of cocoa butter. CBS may be partially hydrogenated, fractionated and/or interesterified to create fats with the desired melting profile and final melting point. Typically, fractionated palm kernel oil is now used to avoid the term hydrogenation on the label.

Lauric fats crystallize directly into a β′ polymorphic form that is stable for extended periods (up to 1 year) under ideal conditions (although palm kernel oil will eventually transform to the more stable β polymorph). For this reason, lauric-based coatings have the advantage of not requiring tempering prior to solidification, although proper cooling conditions must be maintained to ensure rapid crystallization. Specifically, much lower cooling temperatures are required to promote rapid crystallization of CBS coatings than those typically used for cocoa butter chocolate.

Because lauric fats contain nearly 50% lauric acid (C12:0), they are not compatible with cocoa butter, even at very low levels. Coatings made with modified PKO should contain less than about 5% cocoa butter (on a fat basis), otherwise problems during manufacture and storage can arise. The eutectic softening effect that occurs when these two fats mix causes the coating to be undesirably soft and prone to rapid bloom formation. In melt-away candies, the eutectic softening between cocoa butter and CBS is utilized to give a soft texture. Also, coatings for frozen desserts are generally made with coconut oil to provide a softening effect for the low temperature application.

16.2.1.4 Sweetener

In compound coatings, sugar content can be over 50% of the mass of the product. As with chocolates, the important characteristics of the particulate sweetener phase include particle size and distribution, shape, surface properties and sweetness. Typical sweeteners used in coatings include sucrose, inulin, resistant dextrins and lactose along with various sugar-free sweeteners such as maltitol, lactitol, erythritol, stevia and Monk fruit extract. Note that technically, the term sugar-free chocolate is actually a misnomer in the United States because it implies chocolate, but uses an ingredient (e.g., maltitol), a sweetener not accepted in the Standard of Identity. Correct phraseology for this product would be a sugar-free coating.

As with chocolates, the particle size of sugar is important to both rheological properties of the melted coating and sensory attributes during consumption. Generally, particles less than 10 μm or so contribute a significant thickening effect on viscosity, requiring use of higher fat levels. On the other side, if particles are too large, above about 20–25 μm or so, they may be detected in the mouth and impart a coarse mouth feel. Most often, compound coatings are used for enrobing or coating a product, where smooth eating quality is less critical than for molded chocolate. As for chocolate, compound coatings that are molded generally require smaller particle size than coatings used for enrobing.

16.2.1.5 Cocoa Powder

The use of chocolate liquor (with ≈50% cocoa butter) is generally limited in compound coatings by issues of fat compatibility, meaning that the primary chocolate flavor of a chocolate-type coating comes from cocoa powder. However, even cocoa powder contains cocoa butter (usually 10–12%, but may be 22–24% cocoa butter) and so, even the use of cocoa powder may be limited in a compound coating. This is particularly true in coatings made with lauric fats because of the limited compatibility with cocoa butter. A reduced fat cocoa powder (≈5%) may be used in lauric-based coatings to minimize problems of softening and bloom formation.

To combat the softening effect of the cocoa butter present in the cocoa powder, lower levels of cocoa solids nonfat are often seen in coatings compared to chocolate. This will result in a lighter color coating with less chocolate flavor. A common practice is to use a cocoa processed with alkali (Dutched) to give a darker more appealing color.

In white or pastel coatings, no cocoa powder is used at all, meaning there is very little chocolate flavoring to these products. On a positive note, this results in a product that readily accepts other colors and flavors and will not mask them.

16.2.1.6 Dairy Based Powders

Many compound coatings contain milk and/or whey powder. Milk coatings may contain up to 10–15% milk powder, while white coatings may contain even more (15–20%). Milk powders contribute to a dairy flavor and impart an off-white or yellowish color to the coating. However, because of issues with fat compatibility (see

Section 16.4.3), nonfat milk powders are most often used, particularly in lauric-based coatings. Levels of free milk fat mixing with the fat phase of a lauric coating should be less than 3% to prevent problems of softening and bloom formation. Whey powders and lactose may also be used in some compound coatings for reducing sweetness levels and economic reasons. When used, whey powders are often demineralized to remove salts that would otherwise introduce undesirable off-flavors.

16.2.1.7 Nucleator

In certain applications, coating manufacturers add a small amount (≈1% to 3% on the fat phase) of a high-melting nucleator to enhance solidification rates and contraction from molds. These nucleators are often fully hardened vegetable oils (i.e., cottonseed, palm or soy oil) with a melting point greater than 60 °C (140 °F). The purpose of this nucleator is to promote solidification of the coating by increasing the speed of fat crystallization while also raising the melting point. They also reduce solidification time, for example, in a cooling tunnel, enhance contraction from the mold, and enhance appearance (glossy surface). They are particularly effective in coatings where higher levels of cocoa powder introduce more cocoa butter. Certain types of high-melting point emulsifiers may have the same effect.

16.2.1.8 Emulsifiers

Various emulsifiers are added to compound coatings to serve a variety of purposes. Lecithin is still the primary emulsifier used in coatings and it serves the same purpose as in chocolate, to lower viscosity. In the same way as it affects chocolate viscosity (see Section 15.5.3), lecithin acts at the sugar particle-fat interface to reduce particle agglomeration in coatings. The phosphatidyl group of lecithin sits at the hydrophilic surface of the sugar particles with the lipophilic fatty acid groups extending into the fat phase. This prevents the hydrophilic surfaces of the sugar particles from sticking together and allows them to flow more easily across each other under shear forces. The result is a decrease in viscosity on about the same order of magnitude seen in chocolate. That is, addition of 0.5% lecithin results in a viscosity decrease equivalent to adding approximately 5% extra fat (Minifie 1989).

Other emulsifiers may be added to coatings to enhance solidification, improve appearance, and inhibit bloom development during storage (Weyland and Hartel 2008). Sorbitan monostearate (SMS) and mono- and diglycerides (MAG/DAG), specifically glycerol monostearate (GMS), may be used as nucleators to promote solidification and contraction of some lauric-based coatings. Sorbitan tristearate (STS) is widely used in compound coatings as a bloom inhibitor. The specific application and benefits of added emulsifiers vary from coating to coating, so each coating manufacturer has its own standard practices related to emulsifier usage.

16.2.1.9 Flavors

Since there is no Standard of Identity for coatings, there are no restrictions on flavors that can be added. In chocolates, no flavors that mimic chocolate or milk flavors can be added, whereas in coatings, any flavor can be added to enhance the sensory properties. Types of flavors that may be added include caramel, butterscotch, vanilla, yogurt, cinnamon and fruit flavors.

As might be expected, flavors for use in compound coatings should be oil-based or powdered to prevent an increase in viscosity. Flavors are also added near the end of processing to minimize flavor degradation.

A popular compound coating flavorant is peanut butter. Unlike most other coatings where a flavor is added, peanut butter coating will often use a partially defatted peanut flour to reduce the softening tendencies found when using a full fat peanut butter. Salt is also added to enhance the peanut notes. The peanut butter used may also have additional hardening fats added to help reduce the softening effects.

16.2.1.10 Colors

As with flavors, there are no limits on what colors can be added to compound coatings other than those imposed by the physical system itself. Typically, coloring agents like titanium dioxide are added to white coatings for the desired visual effect. As with flavorings, the colors added should be oil based or powdered dyes to prevent an increase in viscosity. Oil-based lake dyes are most often used because of their ease of incorporation. Oil-based dyes need to be mixed well to ensure they are homogeneous since separation may occur upon storage. It should also be noted that the oil carrier for dyes can become rancid upon storage and should be evaluated periodically. While powdered dyes do not have these disadvantages, care must be taken to prevent specking in the finished coating.

16.2.2 Coating Formulations

The diversity of compound coating formulations matches the diversity of applications for which they are used. From molded pieces intended for direct consumption to coatings for granola or nutritional bars, the applications for compound coatings vary widely, as do the requirements for their functionality. Perhaps even more so than for chocolate, control of the physical and sensory properties of coatings are critical to their success. Choices for both ingredients and processing technology must be made carefully, with all key elements, including cost, taken into account.

Table 16.1 summarizes the range of ingredients that are most commonly found in lauric-based compound coatings. Typically, total fat content in compound coatings is 30–35%, about the same as for the fat phase in chocolate. The type of fat depends on the specific application and how much cocoa butter accompanies the use of either chocolate mass or cocoa powder. Furthermore, the fat level also depends to some extent on the type of fat used. Lauric fats tend to give slightly lower viscosity than nonlauric fats at the same usage level, meaning that slightly less lauric fat can be used to target a certain viscosity.

Powdered sweeteners (usually sucrose) makes up the bulk of the coating (40–55%), with the fat making up most of the remainder. Dairy based powder can be used at varying levels. Typically 0–5% is found in dark coatings and 10–15% in ‘milk’ coatings. Cocoa powder usage typically ranges from 5% to 10% for ‘milk’ coating and 10–18% for dark coatings. As mentioned earlier, higher levels of cocoa have a softening effect and a greater tendency for fat bloom. White coatings have a substantial amount of dairy powders (15–20%), but no cocoa powder.

Table 16.1 Typical formulations (in %) for lauric-based compound coatings

Ingredient	Dark	Milk	White	Yogurt
Sweetener	50–55	45–50	50–55	50–55
Lauric fat[a]	29–33	30–34	31–35	31–35
Cocoa powder[b]	10–18	5–10	0	0
Milk or whey[c] powder (nonfat)	0–5	10–15	15–20	0–15
Yogurt powder[d]	0	0	0	0–15
Lecithin	0.2–0.4	0.2–0.4	0.2–0.4	0.2–0.4
Flavor	0.1	0.1	0.1	0–2.0
Color	0	0	0–1	0–1

[a] Modified coconut oil or palm kernel oil
[b] Typically contains 10–12% cocoa butter
[c] Demineralized
[d] May contain cultured skim milk and yogurt cultures

Compound coatings also contain emulsifiers, flavors and may contain colors, especially in the case of pastel coatings.

16.3 Manufacturing

In general, compound coatings are processed through the same steps as used in chocolate (Figure 16.1), although several important differences can be noted (Urbanski 2009). First, the ingredients are mixed together, after which the particle size is reduced through a grinding process, followed by liquification of the paste and standardization prior to use. The coating manufacturer delivers the coating in either liquid or solid form depending on the needs of the end user. Solid coatings can be found in a variety of shapes and sizes, from large blocks to wafers to drops, depending on the eventual application.

The first steps of coating manufacture include mixing the ingredients, except perhaps for a portion of the fat, together into a homogeneous mass

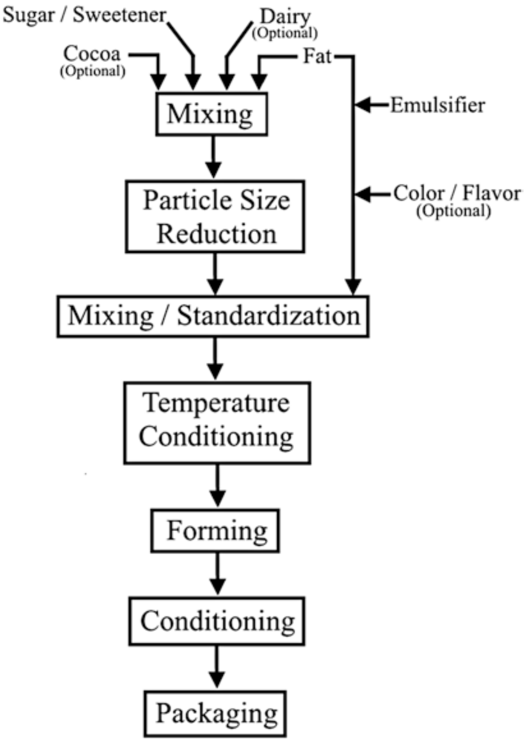


Figure 16.1 Typical processing steps for compound coatings

and reducing particle size. Particle size reduction techniques commonly used for compound coatings include dry grinding methods for powders, roll refiners for paste mixtures, and ball mills for more liquid materials. The amount of fat added to the dry powder mixture is determined by the refining method, from no fat added in dry grinding methods to all the fat being added when ball mills are used for particle size reduction.

In dry refining, the sweetener and other dry ingredients (milk powder, etc.) are blended in the appropriate portions and mixed into a homogenous powder. This powder goes through a classifier mill as described in Section 15.4.8. The powder is fed to a rotating milling disk with hammers, wedges or pins to break the particles to smaller sizes. An air classifier removes small particles while larger ones are retained in the mill until they have been reduced to the desired size. The fine-particulate powder is collected in a cyclone or bag filter, ready for mixing with the other ingredients in the coating formulation.

Another method for grinding particulates in compound coatings is the ball mill. In this case, nearly all the fat is mixed with the powders prior to particle size reduction. The slurry of particles in liquid fat is fed into the ball mill where contacts between steel balls being agitated in the mill cause breakage of the particles. Finished product is withdrawn through a sieve, which retains larger particles within the mill for further particle size reduction. Ball mills can be operated either in batch mode or continuously.

Probably the most common method of particle size reduction in coatings is the roll refiner, the same as used in chocolate processing. For coatings, the dry powders are mixed with sufficient fat to form a thick, wet paste. The paste is fed into the gap between the feed rollers where initial particle size reduction occurs. The paste is sequentially passed through smaller and smaller gaps between the rollers until the final particle size has decreased to the desired level. As in chocolate processing, five-roll refiners are common in the coating industry. Another option available for the manufacture of compound coating is the refiner conche. See Section 15.4.8 for more details of the five-roll refiner and the refiner conche operations.

Regardless of the refining operation, the requirements for particle size reduction in coatings are the same as for chocolate. Particles must be smaller than about 20–25 μm to ensure a smooth eating characteristic, but production of too many particles smaller than 10 μm can have negative effects and require additional fat to maintain viscosity. As found with chocolate, larger particle size can be acceptable when a smooth mouth feel is not required (e.g., coated pretzels) or for economic considerations.

The product exiting the five-roll refiner is a dry paste due to the numerous small particles that have been formed. In chocolate, this refiner paste goes to a high-shear machine, the conche (see Section 15.4.9), where particle de-aggregation, liquefication, water and flavor loss occur. In coatings, only certain of these processes are important and thus, some consider conching to be unnecessary (Urbanski 2009). For one, the dry paste needs to be liquefied, or plasticized, for further use. This may be done in a conche or in large mixing tanks that provide some shearing action. The mixing also ensures de-aggregation of the small particles formed in refining. Additional fat and emulsifier are added here as well to control viscosity to meet the desired specification. Minifie (1989) also claims that cocoa flavor development is enhanced through conching of compound coatings where flavors from the cocoa powder equilibrate with the deodorized fat, whether lauric or nonlauric. Minifie (1989) also states that elevated conche temperatures of 80 °C (176 °F) are beneficial for flavor development in coatings.

Once the coating has been liquefied, it is standardized to the desired viscosity through addition of more fat and/or emulsifiers. When called for in the formulation, colors and flavors are also added in the mixer. At this point, the coating is ready for final disposition, which depends on the size of the user and the ultimate application. For large end users, liquid coating may be shipped in heated vehicles and pumped into storage tanks in the users' facilities. More often, compound coatings are processed into wafers or drops for distribution and use. This process is similar to the belt depositing systems used for making chocolate chips, drops and wafers (see Section 15.4.11.1). After depositing, the coating pieces pass through a cooling tunnel to promote solidification. At the end of the tunnel, the solid pieces are removed from the conveyor and packaged in boxes, bags or totes.

16.4 Applications

Compound coatings are used in much the same way as chocolate, so the discussion on methods of forming chocolate in Section 15.4.11 applies in general to coatings as well. However, several important differences between chocolate and coating may be noted, particularly related to tempering and cooling tunnel requirements.

Tempering requirements for compound coatings depend on the fat being used. Coatings based on CBE require the same tempering as chocolate, since the fats have essentially the same TAG composition and similar polymorphism. In contrast, it is generally considered that both lauric and nonlauric fats used in coatings do not require tempering because they are not polymorphic. Having said that, both types of coatings may sometimes be pre-crystallized to either help speed processing or enhance contraction (and mold release). Lauric-based coatings in particular crystallize rapidly and give good contraction (although not quite as good as chocolate) and generally do not benefit from a tempering process unless other factors become important. For example, lauric-based coatings with higher levels of cocoa butter may benefit from tempering or seeding with hardened fat to offset the inhibition of cocoa butter on fat crystallization. Nonlauric-based coatings crystallize more slowly and contract less from the mold, such that pre-crystallization (or seeding) may often enhance operations (i.e., processing speed, contraction from the mold, etc.).

Coatings are widely used in all forms of molding. Almost any method used for chocolate can be used for compound coatings, although there are certain differences depending on the nature of the fat used in the coating. For one, contraction of a coating piece can be substantially less than for chocolate. When tempered chocolate is solidified, a high percentage of the cocoa butter crystallizes into a stable β V polymorph, giving the necessary extent of contraction, on the order of 9–10%. This contraction allows ready removal of the molded piece from the mold itself. In most cases, the molded piece simply drops out when the mold is inverted. In compound coatings, solidification is not as well controlled and this sometimes causes problems with pieces sticking to the mold. Good contraction requires that a sufficient amount of fat changes state during solidification and that a compact polymorph is formed. Some coating fats do not have the same high solid fat content as cocoa butter, meaning that less fat changes state during solidification. Other coating fats, especially lauric-based fats, crystallize directly into the β′ polymorph, which generally exhibits less contraction due to the looser molecular packing compared to the β polymorph. Either (or both) effects can lead to problems of molded coating pieces sticking to the mold and causing problems with further processing. For this reason, mold temperatures for coatings generally need to be less than used for chocolate.

Although many coatings do not exhibit problems of poor contraction, to circumvent problems in those cases when contraction is limited, a small percentage (2%) of hardened fat or high-melting emulsifiers may be added to the coating fat. These additives are typically called nucleators because they also promote more rapid crystallization, but they also enhance contraction and allow easier demolding. They work best in systems where, for one reason or another, too little fat crystallizes at once to give good contraction.

Compound coatings are also used widely for enrobing candy bars or baked items, where they may even have a decided advantage over chocolate because they do not need to be tempered. Many problems with enrobed chocolate pieces stem from maintaining a constant state of good temper in the chocolate as it forms the curtain through which centers must pass to get enrobed. Coatings generally solidify quickly and directly into the desired polymorph and are thus, relatively easy to use in enrobing operations. In an enrober, melted coatings are simply brought to a few degrees above their melting point prior to forming the curtain. The enrobed pieces then go into a cooling tunnel for solidification.

Cooling tunnel conditions, whether for molded or enrobed pieces, are different for coatings than for chocolate, and cooling conditions are particularly critical for nonhydrogenated coatings. This is again related to the different requirements for fat solidification, particularly the need for maintaining the tempered state in chocolate. If a chocolate piece is cooled too quickly, unstable polymorphs can form at the coldest points near the surface. These unstable polymorphs lead to surface dulling and bloom formation. For this reason, the entrance stages of a cooling tunnel for chocolate need to be relatively warm, say about 15–17 °C (59–62 °F) with minimal air velocity. In contrast, low entrance temperatures with vigorous air movement are used in cooling tunnels for compound coatings to help promote rapid solidification. In particular, nonhydrogenated PKO-based coatings must be cooled rapidly to promote proper crystal formation. Typical temperatures for the different zones of a cooling tunnel for compound coatings are given in Table 16.2. For both lauric and nonlauric-based compound coatings, initial cooling tunnel temperatures are significantly lower than those used for chocolate (see Section 15.4.12). Inlet temperatures between 5 and 8 °C (41 and 46 °F) are common for compound coatings, depending on fat type, as compared to 15–17 °C (59–62 °F) for chocolate. Temperatures in the center of the cooling tunnel can also be cooler for compound coatings since the issue of unstable polymorphism is not a concern. Outlet temperatures for cooling tunnels are again governed by dew point temperatures, with temperatures of 12.8–15.5 °C (55–60 °F) usually being sufficient to prevent moisture condensation as the piece exits the tunnel above the dew point and enters room air. Dwell times for compound coating pieces in a cooling tunnel vary with the nature of the coating, but are typically shorter (about half) than those for chocolates due to the quicker setting.

16.5 Compound Coating Characteristics

In the sense that compound coatings are intended to replace chocolate in many applications, the characteristics desired of compound coatings are generally the same as those desired in chocolate. Some exceptions include applications where coatings can be tailored to actually enhance an

Table 16.2 Typical cooling tunnel temperatures for compound coatings

Zone[a]	Lauric-based coating	Nonlauric-based coating
Initial	5.0–8.0 °C (41–46 °F)	4.4–8.0 °C (40–46 °F)
Center	4.4–7.2 °C (40–45 °F)	2.8–5.5 °C (37–42 °F)
Final (above dew point)	12.8–15.5 °C (55–60 °F)	12.8–15.5 °C (55–60 °F)

[a] Air flow may be vigorous in all sections of the enrober cooling tunnel

application. For example, a compound coating with high melting point may be used in a high-temperature environment or applied to the bottom of a fondant-filled cherry cordial to help prevent leaking.

In particular, the phase behavior and melting properties of the fats used in compound coatings are key elements to successful application. Through careful control of the fat behavior, compound coatings with specific attributes can be made to fulfill specific product needs.

16.5.1 Melting Profile and Fat Modification

Although compound coatings can be tailored for specific applications, in general, the melting properties of the fat in compound coating should match those of cocoa butter (see Figure 15.17) as closely as possible. Specifically, the solid fat content (SFC) at room temperature should be high to give the desired hardness and snap. It should melt quickly over a narrow range of temperatures and be completely melted at mouth temperature. As seen before in Chapter 4 (see Figure 4.15), natural fats like palm kernel and coconut oils, palm oil and butter do not meet each of these specifications, which means that some method of fat modification is required if they are to be used to replace or substitute for cocoa butter. The three methods that are used for processing confectionery fats to improve melting profiles include hydrogenation, fractionation and interesterification. In Chapter 4 (Section 4.5), these technologies were described in detail. In this section, the application of each of these modification technologies for producing fats for compound coatings will be discussed.

16.5.1.1 Hydrogenation

As discussed in Section 4.5.2.1, hydrogenation is the process of saturating unsaturated fatty acids by adding hydrogen to the carbon double bonds. Polyunsaturated fatty acids (i.e., linoleic, linolenic) are converted to monounsaturated fatty acids (oleic and elaidic) and eventually to the fully saturated fatty acid (stearic). Complete hydrogenation of vegetable oils results in essentially all fatty acids being fully saturated; typically, stearic and palmitic acids dominate the TAG composition, with no *trans* fatty acids.

Depending on the fat being hydrogenated and the hydrogenation conditions, different final products can be obtained, many of which find utility in compound coatings. In the past, nonlauric fats were partially hydrogenated under conditions that gave a substantial *trans* fatty acid composition to take advantage of the plastic fat properties of elaidic acid (C18:1 *trans)*. Thus, vegetable oils (soy, cottonseed, etc.) could be partially hydrogenated to give cocoa butter replacers (CBR) for use in compound coatings. Due to concerns regarding the safety of fats containing *trans* fatty acids and changes in regulations, use of this type of CBR has been virtually eliminated.

Full hydrogenation of lauric fats, palm kernel oil (PKO) in particular, can be used in compound coatings to substitute for the majority of cocoa butter. Because of the limited long-chain unsaturated fatty acid composition in PKO, very little (if any) *trans* fatty acids are produced during complete hydrogenation (to Iodine Values less than 4). Thus, completely hydrogenated, or hardened, PKO (HPKO) products have good functional utility in compound coatings. However, the high lauric acid content in HPKO means it is not compatible with cocoa butter. They must be used as substitutes for cocoa butter (CBS), replacing the majority of cocoa butter in the finished product. Also, even though these fats do not have significant levels of *trans* fatty acids, the negative consumer perception of hydrogenation limits their use. Further, complete hydrogenation of PKO raises the melting point temperature above the temperature in the mouth, as seen in Figure 16.2 by the significant SFC value (10%) about 35 °C.

16.5.1.2 Fractionation

Fats with modified properties can be produced by separating specific TAGs of a natural fat based on differences in melting point or solubility in a solvent (see Section 4.5.2.2). The technologies generally used for fractionation of

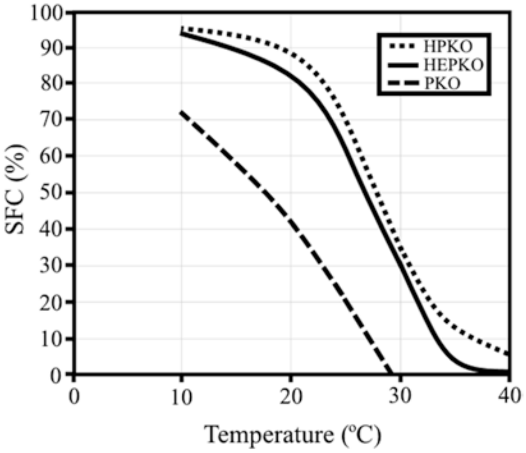


Figure 16.2 Solid fat content (SFC) curves for palm kernel oil (PKO), fully hydrogenated PKO (HPKO), and interesterified HPKO (HEPKO) (Data courtesy of Fuji Vegetable Oil, Inc.)

confectionery fats include dry fractionation and solvent fractionation.

The dry fractionation process involves cooling the molten fat under controlled conditions to crystal a high-melting portion and then separating the crystals from the liquid oil by filtration. The solid material remaining on the filter has higher melting point, with the entire melting profile having higher SFC. This is shown schematically in Figure 16.3, where higher fractionation temperatures are seen to produce stearin fractions with increasing SFC and final melting point. Fractionated palm kernel products, often called palm kernel stearins (PKS), can be made with a range of melting points for use in compound coatings. As seen in Figure 16.4, PKS can be produced that closely mimic the melting profile of cocoa butter.

16.5.1.3 Interesterification

Chemical or enzymatic rearrangement/randomization (see Section 4.5.2.3) of a fat or mixtures of fats can be used to produce confectionery fats with desired melting attributes. A wide range of modified products can be produced based on the nature of the rearrangement (chemical/enzymatic) and the source fat(s). For confectionery fats, chemical interesterification is used almost exclusively. Much of the work on interesterification of confectionery fats is proprietary information, held closely by the fats and oils manufacturers.

16.5.1.4 Combined Methods

To most closely mimic the melting profile of cocoa butter, it is common to use more than one modification technology together. A combination of methods has been increasingly used since the virtual elimination of fats containing *trans* fatty acids. For example, HPKO may be softened to some extent by using interesterification, as seen in Figure 16.2. Specifically, the waxy mouthfeel of HPKO can be reduced through interesterification.

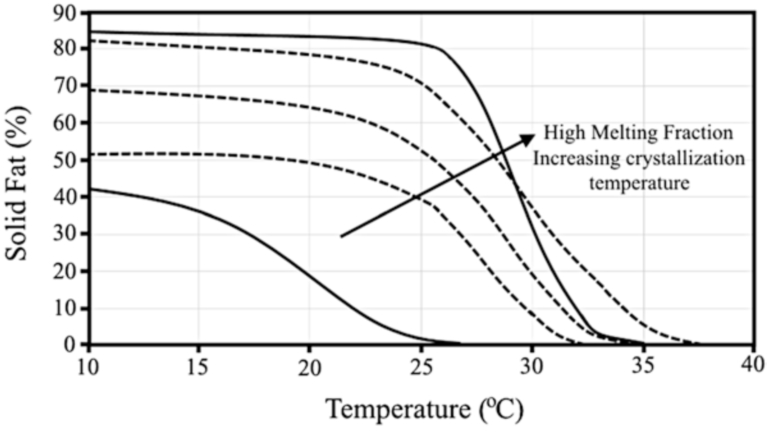
Interesterification might also be used on fractionated PKO, although the advantages are generally limited. Interesterification of PKS actually reduces the SFC over the range from 10 to 25 °C without significantly changing the final melting point.

16.5.2 Phase Behavior

By their nature, compound coatings generally contain mixtures of at least two natural fats – cocoa butter and CBE, CBS or CBR. Since the interactions between fats found in coatings play such an important role, it is necessary to understand the phase behavior when the two fats are mixed. Section 4.3 covers some of the more fundamental aspects of phase behavior and phase diagrams of lipid mixtures, but specific aspects of importance to compound coatings will be covered here.

Of primary importance in compound coatings are the mixtures between cocoa butter and the coating fat, whether CBE, CBR or CBS. As noted in Section 16.2.1, each of these fats has different mixing properties, or compatibility, with cocoa butter. Timms (2003) defined extent of compatibility between two fats based on three properties: (1) thermal properties such as melting point, solid fat content, and heat of melting; (2) molecular size and shape, meaning the type of fatty acids and their arrangement on the TAG; and (3) polymorphic behavior. Two fats that are similar in all

Figure 16.3 Schematic depiction of effects of increasing fractionation temperature on melting properties of a vegetable fat (lower solid line). Upper solid line represents cocoa butter



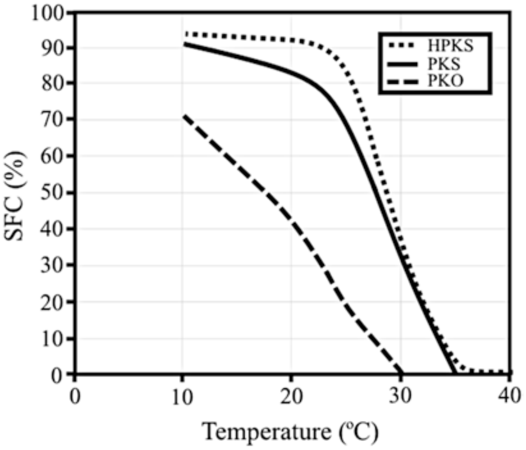


Figure 16.4 Solid fat content (SFC) of palm kernel oil (PKO), fractionated palm kernel oil/stearin (PKS), and hydrogenated PKS (HPKS) (Data courtesy of Fuji Vegetable Oil, Inc.)

three properties exhibit greater compatibility; greater differences in any or all categories indicate greater incompatibility.

By design, CBE have very similar molecular composition as cocoa butter and thus, are considered to be fully compatible with cocoa butter at all addition levels. Based on the isosolid diagram approach covered in Section 4.3.2.3.1, cocoa butter and CBE exhibit an isosolid diagram with essentially flat lines (see Figure 4.13a). The exact mixing behavior between cocoa butter and a CBE depends on the specific TAG composition of the CBE. Bigalli (1988) states that CBE containing higher ratios of SOP and SOS to SOP exhibit perfect compatibility with cocoa butter, whereas those containing higher levels of POP are softer and exhibit a slight eutectic mixing pattern with cocoa butter.

CBR, the nonlauric-based confectionery fats, contain triacylglycerols (TAG) with the same chain length as cocoa butter and are typically considered to mix sufficiently well with cocoa butter up to a level of about 15–20% on a fat basis. Bigalli (1988) presents isosolids diagrams for a *trans*-containing CBR made by hydrogenation and fractionation of a seed oil (soy, palm olein, cottonseed, or rapeseed; source not specified by Bigalli 1988). In this example, addition levels of about 10–15% of CBR to cocoa butter caused little overall change in SFC at almost any temperature (there was a slight decrease in SFC at 21.1 °C). Beyond this level, however, there was a steep drop in SFC at 21.1 and 26.7 °C (70 and 80 °F). This is eutectic fat mixing behavior (as seen schematically in Figure 4.13b) and this sharp drop in SFC is what causes significant softening of the fat blend. The addition of up to 20% cocoa butter to CBR causes only a relatively small (8–10%) decrease in SFC at 21.1, 26.7 and 33.3 °C (70, 80 and 90 °F) with no change in SFC seen at 10 °C (50 °F). It is this behavior that leads people to say CBR is compatible with cocoa butter at up to 20% cocoa butter addition levels. Note that the softest eutectic mixture occurred at a ratio of about 80:20 cocoa butter to CBR. For this mixture level, the eutectic softening effect could be used to advantage to make a melt-away candy center, for example.

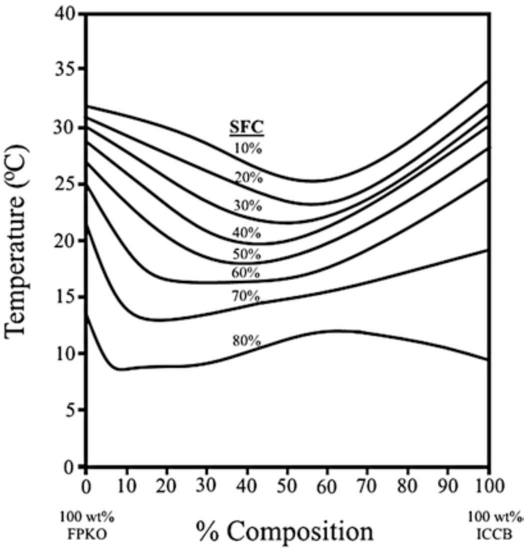


Figure 16.5 Isosolids diagram for a mixture of cocoa butter (ICCB) with a cocoa butter substitute (fractionated palm kernel oil, FPKO) (From Williams 1996)

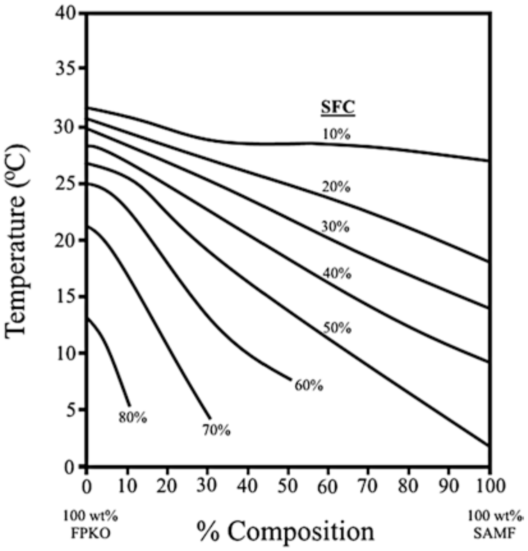


Figure 16.6 Isosolids diagram of a mixture of milk fat (SAMF) with a cocoa butter substitute (fractionated palm kernel oil, FPKO) (From Williams 1996)

CBS made from lauric fats are considered to be even less compatible with cocoa butter than CBR, with addition levels of only 5% cocoa butter on a fat basis to CBS considered to give excessive softening and lead to rapid bloom formation. Figure 16.5, the isosolids diagram for a mixture of a fractionated palm kernel oil and cocoa butter (from Ivory Coast), clearly shows the eutectic softening effect between these two fats. Although the primary eutectic, or the softest mixture, occurs at about a 50:50 blend, there is significant softening that takes place even with less than 10% addition of the cocoa butter to the CBS. In addition to this softening, cocoa butter addition in a CBS-based compound coating causes rapid bloom to occur. For these reasons, it is generally considered unacceptable to have more than 5–6% of cocoa butter in a compound coating on a fat phase basis. This often limits the amount of cocoa powder that can be added to a coating.

Milk fat does not mix well in particular with lauric fats and even a few percent of milk fat in the fat phase can cause problems. Although milk fat and palm kernel oil do not exhibit a clear eutectic (Williams et al. 1997), there apparently is enough mismatch between the triacylglycerols (TAG) of each that just a few percent milk fat in PKO causes significant softening and leads to rapid bloom formation (Ransom-Painter et al. 1997). Figure 16.6 shows the isosolid diagram between anhydrous milk fat (AMF) and a lauric coating (fractionated and hydrogenated PKO). At low levels of addition (<10%) of AMF to this lauric coating fat, there is a significant softening at low temperatures (high SFC levels) even though there is little effect on melting point (lower SFC levels). Addition of AMF to lauric-based coatings also leads to rapid bloom onset. For these reasons, milk fat is rarely found in a lauric-based compound coating. When milk powder is added, it is usually skim milk powder to avoid negative interactions between fats.

16.5.3 Viscosity and Flow Properties

As a high particulate phase volume material, the rheological properties of compound coatings are generally quite similar to those of chocolate, and influenced in the same way by various factors (see Section 15.5.3). Numerous parameters, including moisture, fat content, particle size, number and shape, and emulsifier content and composition, can have significant effects of compound coating rheology.

It is interesting to note that even the composition of the fat can influence viscosity. It is well known that lauric-based coatings typically require less fat to reach a certain viscosity, all else being equal, than nonlauric coatings. That is, inherent properties of the fat, particularly the type and amount of polar lipid impurities present, also influence viscosity.

As with chocolates, compound coatings are made to whatever viscosity specification is needed for the application. The final standardization procedures of adding fat and emulsifier are designed to meet those specifications.

16.6 Shelf Life

Well made compound coatings can last to about a year under proper storage conditions, typically thought to be cool temperatures and low (≤50%) relative humidity. However, even under ideal storage conditions, compound coatings can lose quality. Plus, some question whether cool storage temperatures are always the best – there is some evidence that storage of certain types of coatings at cool temperatures actually promotes bloom.

16.6.1 Sugar Bloom

The same issues that apply for moisture and chocolate (see Section 15.6.1) apply for compound coatings. When moisture contacts the surface of a compound coating, the sugar from within is drawn into the moisture, leaving a mound of whitish sugar crystals when the moisture subsequently dries off. Moisture may be a problem from condensation in humid air or may occur as direct contact (drop of water onto exposed product surface).

Preventing sugar bloom in compound coatings involves eliminating any potential contact with moisture. For example, product exiting the end of a cooling tunnel should have a temperature above the dew point of the air so moisture condensation does not occur. Product that is chilled or even frozen should be well sealed to prevent ingress of moisture through the package and onto the surface. Temperature tempering by moving the product from frozen to refrigerated to ambient temperatures while still tightly packaged can greatly reduce the risk of condensation and subsequent sugar bloom.

16.6.2 Storage Bloom

Some people say that the mechanism for bloom in compound coatings is different from that in chocolate. This comment is usually based on the slight differences in appearance and some interesting differences in conditions that promote bloom in coatings. In particular, some argue that bloom is exacerbated in compound coating when held at 18 °C, rather than at elevated temperatures.

Smith et al. (2004) studied the nature of fat bloom in compound coatings over the temperature range from 15 to 25 °C to help understand why low temperature storage can actually promote bloom in some cases. At 15 and 20 °C, fat bloom scraped from the surface of the coatings was found to contain TAG from both cocoa butter and palm kernel stearin. At 25 °C, bloom was primarily from the palm kernel stearin, with no evidence of cocoa butter TAG. This result was explained based on the phase diagram of the two fats, where a phase separation of cocoa butter was observed if the sample was stored below a certain temperature (see Timms 2003 for more details of this concept).

Often, sorbitan tristearate is added to compound coatings specifically to prevent storage bloom formation. It has proven successful at reducing the rate of bloom formation in both lauric and nonlauric coatings (Laustsen 1991). The exact mechanism for this inhibition is unknown, although it has been hypothesized either to be related to its effect on increasing the density of the fat crystalline structure or to inhibition of the polymorphic transition (Timms 2003).

16.6.3 Moisture Uptake

It should be noted, that as with chocolate, coatings can pick up moisture during storage, even when held under ideal conditions (cool temperature and <50% RH). Because of the higher surface area, coatings deposited in drops, wafers and buttons will exhibit a much larger increase in viscosity upon storage when compared to coating deposited in blocks. As well, there is a much larger increase in viscosity seen with white coatings when compared to dark chocolate over storage time presumably because of the higher sugar and milk powder content.

16.6.4 Rancidity

Oxidative rancidity (see Section 4.2.3.1) is the result of breakdown of fats from the action of oxygen. It is influenced by the chain length of the fatty acids on the TAG as well as the degree of unsaturation. Photooxidation (see Section 4.2.3.2) may also be a concern in some cases. For example, exposure of white coatings to light can lead to oxidative rancidity, with production of off-flavors.

Lauric-based coatings when in contact with moisture and enzymes are particularly prone to hydrolytic rancidity (see Section 4.2.3.2). Here, the enzymes cleave the fatty acids from the TAG, even under the low water-content environment in coatings. The release of soapy flavors as a result of hydrolytic rancidity is more of a problem in lauric coatings than nonlaurics because the threshold detection level of lauric acid is much lower (700 ppm) than that of stearic acid (15,000 ppm).

16.6.5 Off-Flavors

Just as with chocolate, the fat phase of compound coatings is susceptible to picking up various flavors and aromas from the environment. Storage of compound coatings in the vicinity of odorous things like skunks, mint, cleaning compounds and fruity candies leads to rapid transfer of those aroma compounds into the coating, especially if packaging is inadequate to protect against diffusion of these molecules. Transport containers and trailers are often a source of off-flavors and should be inspected for cleanliness and off-odors to reduce this risk. Storage in the refrigerator or freezer is especially problematic due to the abundance of other flavors that can be absorbed by the coating. Proper packaging is needed to reduce off-flavor pick up during long-term storage.

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Chocolate Panning

17

Traditional chocolate panning is the process of applying layers of chocolate coating to inclusions in a rotating pan or drum until the desired coating thickness is reached and the coating has completely solidified. These coated centers are then polished and sealed. Panned chocolate confections have the advantage of being glossy and more resistant to scuffing and melting than enrobed or molded pieces. Here, the phrase 'chocolate panning' will be used, but various forms of compound coatings can also be used with the same equipment to achieve the same approximate finished products.

17.1 Panning Operations

Although called chocolate panning, this process applies to the coating of various centers with either chocolate, compound or yogurt-based coating. The procedures and important points are essentially the same for all three materials. The process of chocolate coating follows the same basic steps as sugar-based coatings (see Chapter 13). After application of a pre-coating (where necessary), multiple layers of chocolate are built up by sequential addition of liquid chocolate followed by adequate time for solidification. While composition may vary somewhat, two parts chocolate to one part center is typical for panned pieces. Equal proportion of coating to centers is sometimes used to reduce cost and, in some instances, to allow part of the center to show through. Once a sufficient chocolate shell has been built up on the center, the pieces are polished and glazed to give an attractive, shiny appearance. The general cross-section of a chocolate-panned confection is shown in Figure 17.1. The four layers put onto the center include pre-coating (optional), chocolate shell, polish, and seal coating layers.

17.1.1 Centers

Centers for chocolate panning come in a wide variety. They may be fruits (raisins, cranberries, etc.), nuts (peanuts, almonds, cashews, etc.), sunflower seeds, coffee beans, specialty centers (cereal pieces, corn nuts, cookie dough, etc.) or candy. Typical candies that may be used include fondant, caramel, malted milk balls, and jelly candies.

For consistent product quality and an efficient operation, the following parameters should be considered and controlled (where possible):

- Size: Center pieces for chocolate panning may be as small as a few millimeters (e.g., sunflower seeds) to as large as a couple centimeters (malted milk balls). Smaller pieces tend to be a little more problematic to coat well, particularly in terms of tumbling action. Probably most important about size is that all the pieces in the pan are about the same size. Having

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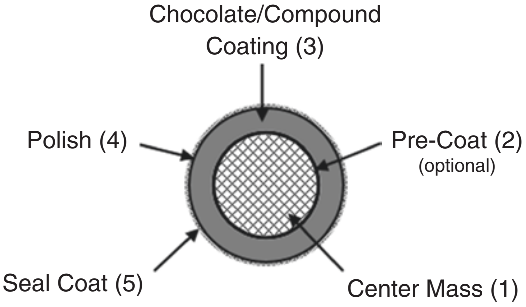


Figure 17.1 Cross-section of typical chocolate-panned candy

consistent sized inclusions makes it easier to maintain individual panned pieces rather than doubles and clusters. It also allows for uniform coating on all pieces. Also, particle segregation within the pan may occur if there are different sized centers, especially in traditional rotating pans.

- Firm texture: Firmer centers make the panning operation more efficient. When panning with soft centers, flexing may occur and the chocolate shell will break away. This is often seen in raisins that are high in moisture or damaged during the cleaning process. Having a smaller bed depth in the pan or pre-coating can help alleviate some of the flexing issues when panning soft centers.
- Density: Center pieces for chocolate panning vary widely in density, from quite low (e.g., malted milk balls) to very high (e.g., almonds). Lighter pieces may result in more problems, particularly if tumbling action is not uniform. Centers should have uniform density to avoid segregation during tumbling.
- Round: Centers should be as round as possible and have minimal flat sides or points. Round centers allow for a uniform spreading of chocolate into a thin layer, uniformly coating the entire piece. It is often difficult to pan centers that have flat sides or points. Centers with flat sides have a tendency to stick together and become doubles. Panning products with pointed ends are often difficult to cover with coating as seen in some almond pieces. This can be solved by using the correct combination of chocolate temperature, viscosity and cooling. Pieces with concave surfaces are notoriously difficult to pan; pre-coating these centers is critical to getting uniform coverage.
- Surface irregularities: Chocolate coating works best on smooth centers, but this is not always possible. Surface irregularities are natural in certain products (e.g., raisins, almonds, coffee/espresso beans, etc.) and must be filled in completely to produce a high quality piece.
- Temperature: To ensure proper setting of the chocolate or coating, the centers should be neither too hot nor too cold. Typically, temperatures between 15 and 25 °C are best. Warmer temperatures do not allow rapid solidification of chocolate, whereas colder temperatures may cause undesired solidification of chocolate into the wrong crystal polymorphic form. Centers should generally be tempered to the panning room temperature.
- Minimal free moisture or fat: Migration of either water or fat into the coating can cause shelf life issues. Moisture is particularly problematic since chocolate does not stick very well to a wet surface, but even liquid oil (e.g., nut oils) can cause adherence problems. These problems are minimized by using a pre-coating layer.
- Dust. Centers should be as free of dust particles as possible. Dust and free powder (often from precoating) should be minimized to prevent an increase in the coating viscosity. This may also lead to an uneven coating shell and small, coated balls of powder that will become waste product.

The ideal center for coating with chocolate would meet all of the above requirements. Unfortunately, most centers for coating with chocolate do not meet all the requirements. In general, the easiest centers to chocolate pan include malted milk balls, caramel balls and round-tipped almonds, with the most difficult being sunflower seeds, espresso beans and cashews.

17.1.2 Chocolates and Coatings

A wide range of coating materials can be found. These include the three main types of chocolate (dark, milk, white) and a variety of compound coatings.

17.1.2.1 Chocolate

Standard of Identity chocolate (see Chapter 15) is often the coating of choice for panned goods. The claim of "real" chocolate on the label is generally a good marketing point. The choice of dark, milk or white chocolate is governed by consumer demands. Many commercial panned products are made with milk chocolate, primarily based on consumer demand. However, dark and white chocolate panned goods are also widely available.

Choice of chocolate for use in panned goods is often based on several factors (Copping 1996). These include the desired quality of the product, based on the target consumer, and at what cost. Viscosity range is also critical (see below for more details). An additional factor is rate of solidification since that is the major determinant in panning times.

Typically, dark chocolate solidifies quite rapidly, but that depends on the nature of the fat phase since cocoa butters from different origins are known to solidify at different rates (Marty-Terrade and Marangoni 2012). Malaysian cocoa butter typically crystallizes more quickly into a harder chocolate than Brazilian cocoa butter, which takes longer to set and gives a softer coating. West African cocoa butter falls between these two, but is generally soft (Copping 1996).

If milk fat is used in the dark chocolate, the rate of solidification is reduced (Metin and Hartel 2012) and the panned layer is softer. Of course, milk chocolate contains milk fat, so it also has a slower rate of crystallization. White chocolate often contains a high level of milk fat and solidifies at a slower rate. In fact, white chocolate is generally quite soft and may be harder to work with than dark or milk chocolate.

17.1.2.2 Compound Coatings

Numerous choices are available if Standard of Identity chocolate is not needed. Compound coatings (see Chapter 16) come in a wide range of flavors, types and formats. In addition to the standard dark, milk and white coatings, other choices include yogurt or carob-based coatings.

Several advantages arise from using compound coating for panned goods over chocolate-based coatings. First, greater control over the fat phase is possible, with a wider range of melting points and solidification rates. The confectioner can select coatings with specific fat composition to enhance solidification rates and control coating hardness. A second advantage is the possibility of adding colors and flavors. However, one of the usual advantages of compound coatings over chocolate, namely that tempering is not needed, does not apply in panning since chocolate can be applied untempered with no negative effects.

Similar factors as discussed above influence choice of coating for panned goods. Quality, consumer demand and cost are still primary choices, as is rate of solidification. Again, the confectioner has a wide range of options from which to choose to find the best coating for use in panned goods.

17.1.3 Pre-coating

Pre-coating needs for different centers depend on the nature of the surface to be coated with chocolate. Of particular concern are moisture (e.g., fruits) and incompatible oils (e.g., nuts), which must not be allowed to come in direct contact with the chocolate coating. If such products are not pre-coated, the candy maker runs the risk of having bloomed product as both moisture and nut oils can migrate into the shell coating and lead to bloom.

Pre-coating of centers for chocolate panning, as with sugar panning (see Section 13.2.2), typically calls for application of a gum or starch solution followed by dry powder addition to seal the center. Regardless of whether the pre-coat is intended to protect against moisture or oil migration, the solution component is typically gum arabic or modified starch. These provide decent barrier properties against both moisture and oil. The pre-coat solution must be at the appropriate viscosity to give good coverage of the center. Typically, solutions of 40–50% dissolved solids content are used. Several layers of coating solution are applied to the centers tumbling in the pan, with dry powder addition between each solution application. Dry powders added may include starch, sugar or cocoa powder. After the pre-coat has been applied and allowed to dry, the chocolate coating application can begin.

17.1.4 Chocolate Coating Application

To ensure good coating and solidification of the chocolate shell, the temperature and relative humidity (RH) of the air applied into the pan must be controlled to insure consistent successful panning. The exact air temperature and RH will be dependent on the coating, centers and equipment, but generally range from 7 to 15.5 °C (45–60 °F) and 35–50% RH. It is essential that there is no condensation of moisture from the air to the product.

Melted chocolate or coating is applied at a temperature that depends on the application method. For chocolate, hand ladling is applied at 32–35 °C (90–95 °F), whereas ≈40.5 °C (105 °F) and ≈43 °C (110 °F) are used for drip and spray nozzle applications, respectively. Compound coatings are usually applied slightly warmer (as high as 46 °C/115 °F) to achieve a smooth finish. Chocolate need not be tempered prior to application in panning since the tumbling process promotes formation of stable cocoa butter polymorphs (see Section 15.5.5) and bloom is usually not a problem. When tempered chocolate is used, it will usually set too fast, resulting in an uneven, rough coat and excessive adherence to the sides of the pan.

A critical parameter to control in chocolate coating, as in sugar coating, is the viscosity of the coating material. Viscosity of chocolate or coating must be of the right fluidity to provide adequate and complete coverage of the pieces. Chocolate is a non-Newtonian fluid and there are two parameters, yield stress and plastic viscosity, that govern flow and coating ability (see Chapter 15 for more details). In panning, both parameters are important, although the yield value, or the force required to initiate flow in the chocolate, is critical to the thickness of the shell being applied (Aebi 2009). Viscosity must not be too low or the centers will not tumble well in the pan nor will sharp edges (on almonds for example) be adequately covered. Conversely viscosity must also not be too high or inconsistent coverage of the centers will occur. Furthermore, application of high viscosity chocolate will cause excessive coating on the inside of the pan, resulting in ingredient losses. The main parameters that affect chocolate viscosity are temperature, fat content, emulsifier type and content, moisture content and particle size of the chocolate or coating. These must be controlled to give the desired viscosity for proper chocolate panning. See Chapter 15 for more details on the effects of these parameters on chocolate viscosity.

Typical viscosity values for chocolates and coatings used depend on the centers being panned, equipment used, and air and room temperatures/relative humidity. However, target values are about 70 Poise (7,000 cP), with a range from 50 to 90 Poise (5,000–9,000 cP; or approximately 35–45 Brookfield reading using the NCA viscosity method; Copping 1996). As noted above, chocolate with a yield stress on the lower side is preferred for panning work to ensure proper spreading of each application onto the center.

Chocolate may be applied by either hand ladling, drip feeding or spray nozzle, depending to some extent on the size of the candy facility. Typically, smaller facilities tend to use hand application and larger facilities favor drip feeding or spraying. Hand ladling involves application of the proper dose of chocolate along (front to back) the base near the top of the tumbling mass in the pan. In drip feeding, the chocolate is pumped through pipes to nozzles just above the bed of tumbling centers in the pan, where the chocolate is allowed to drip onto the centers. Spray feeding requires pumping the chocolate to a spray nozzle where the liquid coating is atomized to coat the centers. The spray nozzle is mounted above the tumbling centers in the pan with the chocolate spray aimed at the tumbling pieces. The advantage of the spray nozzle is that it greatly reduces the tendency to form doubles (or clumping); however, care is needed to ensure that the chocolate does not cool in the nozzle to plug up the lines. Further, the spray pattern must be controlled to achieve even coating. Regardless of the method of chocolate application, but especially in spray or drip feeding, proper temperature control of the coating is critical to good panning (adequate coverage without excessive clumping).

To build the chocolate shell in panning, sequential doses of chocolate are applied to the tumbling centers with each liquid application followed by a period of cooling and solidification. The amount of coating used in each application dose must be high enough to ensure good surface coverage without being too large to cause excessive clumping of the centers. Groves (1992) suggests starting with 2.5 kg (5–6 lb) of chocolate per 45.5 kg (100 lb) of centers, increasing to 4 kg (8–9 lb) per 45.5 kg (100 lb) of centers as the shells builds and surface area increases. These numbers must be modified slightly for different initial surface areas of the centers. After application of the liquid chocolate and sufficient coverage of the centers, cooling air is blown into the pan to promote solidification. Spray systems generally have air blowing at the same time, and the chocolate spray is constantly on throughout the run.

As mentioned earlier, air conditions are important to making high-quality chocolate panned products. Room air should be cool (15.5–18.4 °C; 60–65 °F) and reasonably dry (40–55% RH). Cooling air directed into the pan is generally cooler (7–15.5 °C; 45–60 °F) and drier (<35–50% RH) to ensure proper solidification without the risk of moisture condensation. The air should be filtered to insure products are safe from microbiological or other contaminants. Air velocity must also be controlled since cooling requirements may be different depending on the stage of panning. Generally, a recommended air flow rate is 500–850 m^3 per hour (300–500 ft^3 per minute). Chocolate panning under adverse conditions (warm, humid air) generally results in poor quality products with low production output.

Typically, from 5 to 10 min is needed to ensure adequate solidification of one layer prior to application of the next dose of chocolate. Coating materials should be selected with solidification rate in mind. The application and solidification cycle continues until the desired shell layer is built up on the piece, with panning times anywhere from 0.75 to 2 h. More rapid solidification can be induced by use of a vaporizing refrigerant like carbon dioxide (dry ice) or nitrogen, although this leads to a rough surface that must be smoothed out by tumbling the pieces in the pan to allow frictional heat to melt the rough spots. Furthermore, release of compressed gases requires that safety and environmental codes be satisfied. Condensation can also occur when using this method, which will result in the shell to soften.

Often, a smoothing step is used to ensure an even coating with a smooth surface. Here, the pan is tumbled without air flow to allow any irregular chocolate surface structures to become smoothed out.

Once the desired chocolate shell has been applied, the candies are often held in pans to allow for sufficient solidification time to provide a good base for finishing. When ready, the candies are returned to the pan for polishing and glazing. Some of the large automated panning systems have eliminated this solidification step.

17.2 Pan Types

There are three basic systems for panning: conventional or traditional revolving pans, belt coaters and automated pans. All three methods of panning follow the same basic procedures and processes of building a coating layer, polishing and sealing coating.

Conventional revolving pans (Figure 17.2) come in various sizes and shapes but most common are the round pans and tulip pans. These pans are usually at an angle (about 25°), sometimes with a variable pan rotation speed. The pan rotational speed depends on the pan size and design, the type of centers that are being panned and whether the process is building the chocolate layer or the final polishing stage. Traditional panning rooms have one set of pans for building the coating layer (engrossing) and another set of pans (ribbed) for polishing and final seal coating. While conventional pans are very versatile and economical, they require more operator skill and production is more limited (160–225 kg; 350–500 lb) than panning with a belt or automated drum pans.

Belt coaters are widely used for chocolate panning (Figure 17.3). Belt coaters have an endless belt that forms a ‘pocket’ for the centers to be

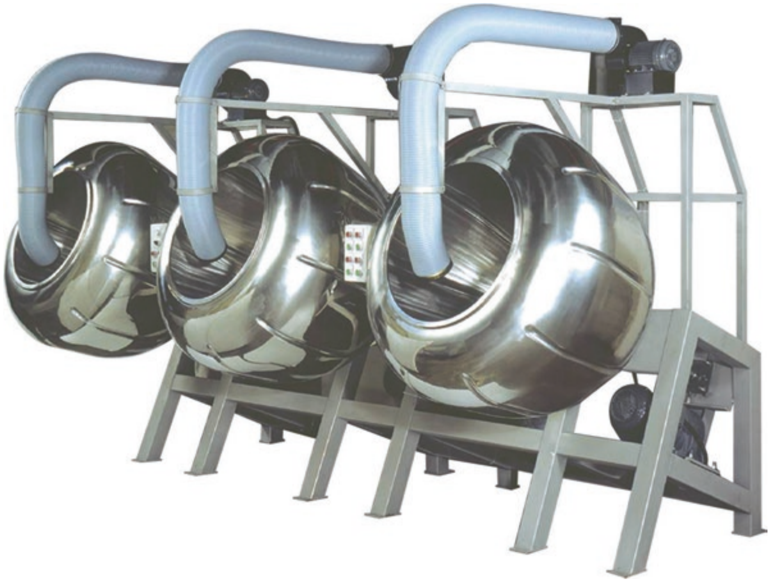


Figure 17.2 Typical tulip-shaped revolving pan (Courtesy of Latini)

Figure 17.3 Belt coater for chocolate panning (Courtesy of Schebler)

coated. The movement of the belt causes the product to fall back upon itself to cause the rotational effect to build up the chocolate layer as the chocolate is applied. After engrossing, the belt is reversed to unload the product. It is then transferred to rotating pans or another belt coater for polishing and sealing. Production volumes are usually higher than rotating pans, but lower than automated pans. Ranges from 225 to 450 kg (500–1000 lb) are common. These pans are well

Figure 17.4 Chocolate coating drum (Courtesy of Dumoulin)

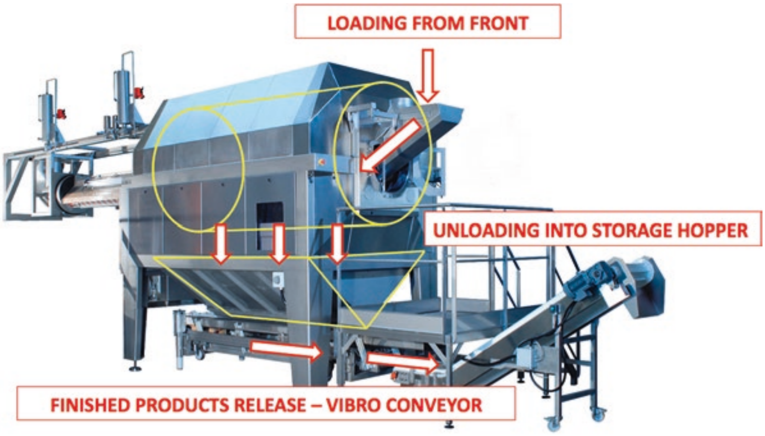
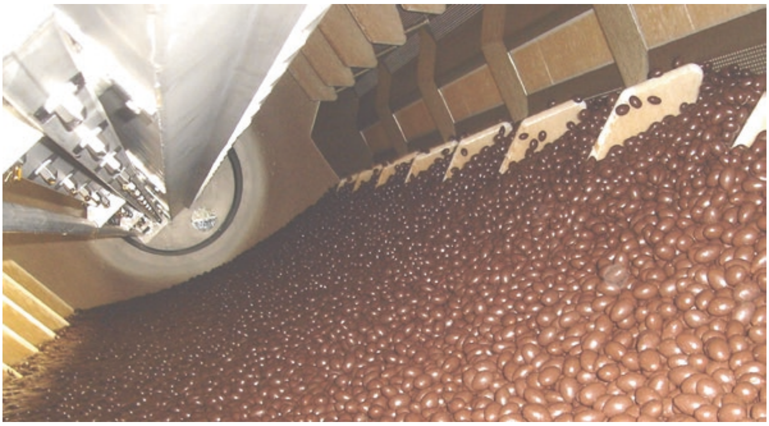


Figure 17.5 Inside of a drum coater showing tumbling pieces. Spray nozzles (not operating) can be seen at *upper left*, above the candy pieces (Courtesy of Dumoulin)



suited for the midsized manufacturer that wants economical, consistent product with less operator artisanal skill required. Polishing results with a belt coater may be more challenging than with a revolving pan.

Automated pans have a large rotating drum with controlled conditions that can supply the needed powders, coating, polishing, conditioned air and sealing agents in a precise manner. They are self-contained units with spray bars, nozzles, feeders, baffles and vents to accomplish this (Figure 17.4). Figure 17.5 provides a glimpse of product tumbling in a drum coater. With their large size, it is possible to have a smaller bed depth that will prevent crushing of centers that are fragile or flexible such as seeds or raisins. While many of the automated pans use one drum for engrossing and one for polishing and sealing, it is possible to do all these operations in one drum. Typical batch sizes for automated pans range from 450 to 2270 kg (1000–5000 lb).

While all three methods can produce high quality candy, product quality will always be dependent upon the consistency of the starting materials, operating conditions, and operator skill.

17.3 Finishing

Once the center has been coated, various finishing options may be chosen. The standard finish is to polish and glaze, but other options exist. These include finishing with powdered sugar, cocoa, a hard sugar-shell, spices, or speckling.

17.3.1 Polishing

Polishing of panned products creates a glossy appearance for customer appeal. A glossy appearance cannot occur unless the panned centers are smooth, firm and free of dust. For batch revolving pans the centers are put into a ribbed pan so that the pieces can be picked up by the sides of the pan to provide adequate tumbling action. This tumbling action with a polishing agent causes a shiny gloss to the finished product. Polishing agents are usually water based and include gums, starches or dextrins. While they can be made in-house, they can also be purchased premade with a blend that contains the desired properties. The dosage for polishing materials depends on its formulation, the size of the centers and equipment used. Typical starting point is 0.20–0.50% polishing solution that is usually about 60% solids.

The polishing solution is applied to the centers and the pan is rotated to evenly spread the solution. Conditioned air is then applied to dry the solution and develop a gloss while tumbling. Two to three doses are usually required to develop a sufficient sheen.

17.3.2 Glaze Coat

Once an acceptable gloss has been obtained it must be protected. The most common method to maintain gloss, provide a moisture barrier and to a small degree some heat resistance to the coating is to use confectioners glaze. Confectioners glaze is an edible shellac dissolved in alcohol that may also contain other minor functional ingredients.

The traditional method is to apply approximately 0.15–0.20% seal coat to the centers and rotate the pan until they are coated. Rotation is stopped and conditioned air is applied to dry the glaze coat. The pans are occasionally turned to prevent massive clumping. When dry, the rotation of the pan resumes for a short time to remove “kiss-marks”. The addition of other ingredients to the confectioners glaze, such as oils or mono and diglycerides, will allow for continuous rotation of the pans to seal coat the centers. While seldom used in present panning operations, the use of waxes (beeswax or carnauba) can be used as an alternative to confectioners glaze.

17.3.3 Hard Sugar Shell

Some chocolate panned items will be finished with a sugar shell instead of the typical high gloss appearance. This procedure will make the finished product somewhat heat stable and is often seen on seasonal products such as Robins egg malted milk balls. Chocolate-coated nuts and seeds often have a hard panned sugar shell applied to the outside (Chapter 13). As with any sugar panned chocolate product, panning conditions require temperatures below the melting point of the chocolate layer. It is common to apply polish and glaze layers to the hard panned sugar shell in the same manner described above, but using a wax-based polish rather than a water-based polish.

17.3.4 Powdered Finishes

While the majority of panned items are polished and seal coated for a glossy appearance, some are made with a ‘matte’ finish. After the engrossing steps are completed and the product has a smooth surface, a powder such as cocoa or sugar is introduced into the rotating pan. These powders, sprinkled onto the last layer of chocolate application, are incorporated into the coating layer by the tumbling forces to give the desired finished appearance.

17.4 Storage and Handling

After the panning process is completed the centers are often stored in pans or totes before packaging. They are typically stored in an area with a temperature range of 15.5–20 °C (60–68 °F) with a RH of 40–50%. Higher RH will result in the pieces sticking together while a lower RH can result in the cracking of the seal coat due to drying. Gentle handling techniques should be employed until the panned confections are packaged where they will have protection from the environment.

Like other chocolate items, they should be stored in sealed packaging with good moisture and oxygen barriers. Storage conditions should be odor free with typical temperatures of 18 ± 2 °C (64 ± 4 °F) with a RH of 45 ± 5%. While chocolate-panned items are more resistant to heat than molded and enrobed chocolate pieces, extreme heat exposure will cause fat bloom and product deformation.

17.5 Trouble Shooting

Consumers expect a consistent high quality product. As in any operation, there are challenges that can result in unacceptable product. The following are some common defects found with chocolate panning and suggested solutions needed to correct the problems (Copping 1996).

17.5.1 Incomplete Coverage

If the pieces are not completely coated with chocolate coating, leaving bare spots, it is likely that the coating was either applied at too low a ratio (coating to center ratio) for the surface area of pieces or it was not able to adequately spread before it cooled and set. If the proper level of chocolate coating was added, perhaps the viscosity of the coating was too high and/or its temperature was too low. Increasing temperature might eliminate the problem. Air flow and temperature may also be the problem, causing the chocolate coating to solidify too rapidly, before it could spread evenly. A pan that is rotating too slowly could also contribute to this problem.

17.5.2 Poor Coverage

Pieces that are not evenly covered could be caused by uneven centers or a low coating to center ratio. For centers that are not uniform in shape or have cracks and crevices, a good pre-coating layer application can help smooth out the surface onto which the chocolate coating is applied. Increasing the amount of chocolate coating applied or reducing coating viscosity might also help spread the coating uniformly before it solidifies.

Exposed surfaces may also be caused by sharp edges, such as the point edge of an almond. If rounded-tip almonds cannot be used, alternatives include ensuring there is good pre-coat for the chocolate coating to adhere to and that the viscosity of the coating is properly set. If the chocolate coating is too warm, it will not adhere to that sharp point. Making sure that the first applied chocolate layers are well set will also help.

17.5.3 Bumpy/Rough Surface

When the chocolate coating layer is rough or bumpy, several factors may be considered. For one, the chocolate coating could be too thick so that it does not spread uniformly before it begins to set. Raising the temperature of the chocolate coating will help reduce viscosity and smooth out the applied layer. Air that is too cold could also cause a rough surface by causing too rapid solidification of the chocolate coating. Rough surfaces may be smoothed out by turning off the cold air and allowing the pieces to tumble. The heat generated during tumbling will soften the coating, allowing it to smooth out.

17.5.4 Chocolate Not Sticking/Peeling

Probably the main cause of a chocolate coating either not sticking or peeling off the center is the lack of a pre-coat. When a chocolate coating is applied on top of a moist surface (as in some fruit centers), it will not adhere to the surface. A good layer of pre-coating to bridge between oil and water should allow the first layer of chocolate coating to adhere and help the problem.

Chocolate coating not sticking to the center can also be caused by too thin a viscosity. Possible causes of this might include coating temperature too high, air temperatures too high or centers being too warm. Other potential causes include pan speed too high, centers too soft, or a heavy load in the pan.

17.5.5 Doubles

A common problem is that pieces stick together to form doubles or even clusters. Not allowing the chocolate to solidify properly before adding more is the most likely reason. Another common cause of doubles is that the chocolate coating is added too fast so that it does not spread into a uniformly thin layer. The proper coating to center ratio is required for proper pan operation. Doubles may also be caused by a chocolate coating that is too thick. Reducing viscosity, for example by raising the coating temperature, or switching to a spray system can both potentially help this problem. Pieces sticking together may also be caused by a pan that is turning too slowly. Check that proper pan rotational speed is being used.

17.5.6 Crushed Centers

Centers that break during application of a chocolate coating are generally caused by having too heavy a load in the pan for the sensitivity of the center. Reducing pan load should help.

17.5.7 Bloomed Pieces

Although bloom on panned chocolate pieces is rare, there are some instances when bloom can appear on panned goods. This is usually related to incompatible fat systems; for example, a nut oil migrating into a chocolate shell. To prevent this, a good pre-coat layer is needed to help limit migration. Another possible source of fat bloom is storage or transportation conditions that are too warm.

Although numerous problems can arise in chocolate coating, it is actually considered the easiest panning method to learn. In general, chocolate coatings are relatively forgiving and problems more easily rectified.

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Glossary

Absorption Moisture uptake; when candy gains moisture from surrounding air.

Aldehyde An organic molecule with the general formula R-C(=O)H group, containing a carbonyl group (C=O double bond) and an additional carbon compound, R.

Alkalization Process of raising the pH of chocolate components (cocoa, nib, liquor) to manipulate color and flavoring; also called Dutch processing.

Alkaloid Chemical compounds found in chocolate – theobromine and caffeine.

Amorphous A state of material where the molecules have a random arrangement.

Apparent viscosity The instantaneous viscosity of a material; defined as shear stress over shear rate.

Autoxidation A mechanism of lipid oxidation based on the presence of oxygen.

Baumé Units used to designate specific gravity of glucose syrups.

Belt coater Semiautomatic method of panning using an endless belt to provide the tumbling action to coat centers.

Binder (1) Solution, often made of corn syrup and a stabilizer (gelatin, gum arabic, etc.), that holds particles together in a wet granulation for making tablets. (2) Dry material (gelatin, etc.) that holds particles together in dry granulation process for making tablets.

Binding forces The intergranular forces, usually from binder solution, that hold a granule together.

Bloom Undesirable formation on the surface (and sometimes interior) of chocolate; may be either sugar or fat bloom.

Bloom strength Firmness rating for gelatin gels, based on the weight required to depress a plunger into a 6.67 % gel a distance of 4 mm.

Bob syrup A thinning syrup that dilutes fondant to allow for depositing.

Bonding The forces, both physical and chemical, that holds particles/granules together within a tablet.

ºBrix Units used to designate sugar syrup concentration based on equivalent sucrose concentrations (measured by refractive index).

Bulk density Mass of powder particles in a unit volume, where the volume includes particles, inter-particle void volume, and internal pore volume.

Butyl rubber (IIR) An elastomer found in gum base; a co-polymer of isobutylene and isoprene.

Caramel A chewy confection comprised of sugars and milk ingredients, characterized by browning due to heating of sugars and/or milk ingredients.

Carr's index A dimensionless number that provides an indicator of how well a powder will compress.

Casson model A rheological constitutive equation that defines the relationship between shear stress and shear rate; see Equation 15.1.

Chocolate panning The coating of centers with chocolate with a tumbling action to produce round individual pieces.

Cocoa butter equivalent (CBE) A natural fat that has nearly identical chemical composition and physical properties as cocoa butter. CBC have a high compatibility with cocoa butter.

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Cocoa butter replacer (CBR) Natural fats (nonlauric) that can be used to replace a portion of cocoa butter in a compound coating.

Cocoa butter substitute (CBS) Natural fats (lauric) that can be substituted for nearly all of the cocoa butter in a compound coating.

Cold flow The ability of a confection to flow, or change shape, at room temperature. In caramel and fudge, structural elements including protein aggregates, fat globules and sugar crystals dispersed through the matrix helps prevent cold flow of the amorphous mass.

Compaction Production of a tablet from a powder by application of pressure, compression.

Conche High torque mixing machinery for smoothing flavors, reducing moisture and viscosity of chocolate.

Critical micelle concentration (CMC) The concentration of emulsifier where no further reduction of interfacial tension is observed and above which micelles form.

Crystallinity Relative mass of a confection that is crystalline.

Deliquesence The ability of a solid (crystalline) material to pick up moisture and dissolve into a liquid.

Deliquescent point Relative humidity at which a solid is dissolved by water vapor in the air.

Denaturation Loss of secondary, tertiary and quaternary structure of a protein through unfolding of a protein structure, usually caused by heat, but also may be caused by pH changes, addition of salts or organic solvents.

Density Weight per unit volume, given in units of g/ml.

Desorption Drying out; when candy loses moisture to surrounding air.

Dextrose equivalent A measure of the reducing power of a starch solution, calculated in terms of the equivalent reducing power of glucose (dextrose).

Differential scanning calorimeter (DSC) A device for quantifying enthalpy changes of a sample relative to a reference.

Diffusion Molecular movement from a region of higher concentration (activity) to lower concentration (activity).

Doctor An ingredient added to a confection to control sucrose crystallization (i.e., glucose syrup, invert sugar, etc.).

Dropping point temperature The temperature when a solidified fat softens to the point where a spherical droplet begins to sag.

Drum coater A large volume self-contained revolving drum used for panning; usually programmed to automatically control the process and require minimal operator input.

Dry charge The application of powdered sweetener to a center in soft panning.

Dye A molecule dissolved in water that absorbs certain wavelengths of light to produce a visible color.

Encapsulation A method of protecting flavor, sweetener or active ingredients to control release.

Engrossing The process of building layers on a center during the panning process before polishing and sealing occur.

Engrossing syrup Sweetener syrup applied to centers in a pan.

Enrobing The process of putting a layer around a piece by passing the center through a curtain of liquid coating.

Equilibrium relative humidity (ERH) The relative humidity at which a candy neither gains nor loses moisture.

Fat bloom Surface discoloration (and sometimes interior) of chocolate and compound coatings caused by fat recrystallization.

Frappe' A protein-stabilized foam or whip with a low density (≈0.2–0.3 g/ml) used to aerate confections.

Fudge Technically a grained caramel. A highly grained confection containing sugars and milk ingredients with sufficient sugar crystals to provide a short, soft texture.

Fugacity Thermodynamic property related to the “escaping tendency” of a gas.

Gelatinization The process of hydrating and disrupting (or fracturing) starch granules in excess water. See *Pasting*

Glass An amorphous state of matter characterized by a sufficiently high viscosity that a glass has solid-like properties.

Glass transition temperature, T_g The temperature (or range of temperatures) over which a material goes from being more fluid-like to more solid-like (and vice-versa). Typically thought to occur when viscosity is about 10^{12}–10^{14} kPa-s.

Glazing The process of applying components that seal the surface of a panned candy from environmental factors.

Glyceride (or acyglycerol) Esters formed from glycerol and fatty acids.

Graining factor Ratio of crystallizing sugar to total sugar content.

Granule Particle made of aggregated crystals of base material, held together by binder.

Gum base Complex mixture of elastomers and other components (as defined in FDA Code of Federal Regulations) that provides chewing and bubble-blowing characteristics to gum.

Hardness The resistance of a material (such as a tablet) against penetration into the surface.

Hard panning The process of putting a hard, brittle sugar shell on a center.

Heat of dilution The enthalpy change associated with the addition of a solvent to a solution.

Heat of solution The enthalpy change associated with dissolution of a solid substance in solvent, which typically involves three stages: (1) breaking solute-solute attractions (endothermic), (2) breaking solvent-solvent interactions (endothermic) and (3) forming solvent-solute interactions (exothermic).

HSH/hydrogenated starch hydrolysate A sugar free hydrogenated glucose syrup or sugar alcohol version of glucose syrup.

Humectant A substance that promotes retention of water.

Hydrocolloid A substance that forms a gel with water (see Chapter 5).

Hydrophillic-lipophillic balance (HLB) A scale used for emulsifiers telling whether it is more hydrophilic or lipophilic.

Hygroscopic The characteristic of rapidly picking up moisture from the air.

Iodine value A measure of the degree of unsaturation of a fat. High values mean more unsaturated fats.

Interfacial (surface) tension The force of the molecules at the surface of either air-water or oil-water interface.

Ionic strength A measure of the number of ionic species (dissociated salts, etc.) present in a solution.

Isoelectric point The pH at which point there is a net zero charge on a protein. At this point, proteins aggregate and precipitate out of solution.

Inversion The hydrolysis of sucrose into its constituent monosaccharides, glucose and fructose.

Invert sugar/syrup The syrup resulting from complete hydrolysis of sucrose into glucose and fructose.

Invertase An enzyme that hydrolyzes sucrose into fructose and glucose to make invert sugar syrup.

Jujube A fruit-flavored gum drop that typically has a low moisture content and a firm gel.

Ketone An organic molecule with the general formula RC(=O)R' containing a carbonyl group (C=O double bond) and additional carbon compounds, R and R'.

Lake A particulate form of color with dye molecules bound to an alumina particle.

Lauric fat Natural fat with a high content of lauric acid (C-12), namely palm kernel oil and coconut oil.

Lecithin An emulsifier, or an amphiphilic molecule, containing phosphatidyl polar groups and fatty acid alkyl groups; used to reduce viscosity in chocolate and compound coatings.

Licorice A chewy flour-based confection that contains extract of licorice root.

Lipolysis Breakdown of glycerides into fatty acids, often caused by enzymes in foods.

Lozenge Product made by binding particles together with a mucilage (or binder) followed by drying to make a hard product.

Milk crumb A dairy ingredient in chocolate made by cooking milk solids and sugar (and sometimes chocolate liquor).

Nonlauric fat Natural fat that does not contain high levels of lauric acid; namely, soybean, cottonseed, palm oil, etc.

Nuclear Magnetic Resonance (NMR) Method of measuring solid fat content based on difference in response to electromagnetic pulses between liquid and crystal molecules.

Optical rotation The ability of sugar molecules to rotate a plane of polarized light.

Partition coefficient Relative concentration of flavor in hydrophobic phase (gum base) compared to water (or saliva) at equilibrium.

Pasting The process of disruption of the crystalline nature of a starch granule by addition of water and heat. See *Gelatinization.*

Peptide A series of several amino acids in a sequence; generally shorter in size than a protein.

Peroxide value Content of peroxides in a fat, representing the level of primary oxidation.

PGPR, polyglycerol polyricinoleate An emulsifier, or a amphiphilic molecule, made from polymerized glycerol and polymerized ricinoleic acid; used to reduce viscosity, and yield stress in particular, of liquid chocolate and coatings.

Pigment Insoluble substance that imparts color through the dispersion of light.

Plastic viscosity Apparent viscosity of liquid chocolate after steady flow has been achieved.

Polishing The process of applying components that provide a shiny appearance to panned goods.

Polymorphism The ability of a molecule to take different crystalline structures.

Polyisobutylene (PIB) An elastomer found in gum base; a polymer of isobutylene.

Polyol A sugar free ingredient produced by hydrogenation of a sugar to yield a sugar alcohol.

Psychrometric chart Thermodynamic diagram that correlates properties of water vapor.

Reducing sugar A sugar that contains an aldehyde group or is capable of forming one. It forms two isomers in solution, the α and β forms.

Refining The process of breaking particles (sugar crystals, cocoa solids) into small sizes to create a smooth chocolate.

Refractive index Ratio of speed of light in air to that in a sugar solution; used as a measure of sugar concentration.

Reversion The polymerization of monosaccharides into longer chain molecules at conditions of high temperature and reduced pH.

Rework Typically, hygienic product of unacceptable quality to be reused in a subsequent batch.

Rheology The science of flow of materials.

Roasting The process of heating cocoa beans, nibs or chocolate liquor to bring out the chocolate flavors.

Shear rate Velocity gradient within a sheared fluid, set up by applied shear stress.

Shear stress Stress applied to cause flow of liquid chocolate; defined as force over area.

Shear thinning A rheological behavior that appears as a decrease in apparent viscosity at higher shear rates; also called pseudoplastic behavior.

Slip point A measure of melt point of a fat based on the temperature when a column of solidified fat in a capillary begins to rise (due to buoyancy) as temperature is increased.

sn-1,2,3 The three carbon bonding sites on a glycerol molecule, used to indicate where each fatty acid is located on a glyceride

Soft panning The process of putting a soft sugar shell on a center.

Solid fat content (SFC) The amount of fat crystals in a partially crystalline fat, based on direct measurement by Nuclear Magnetic Resonance (NMR).

Solid fat index (SFI) The relative amount of crystals in a partially crystalline fat, as measured by dilatometry. Note that SFI has been largely replaced by the more accurate SFC.

Specific gravity The relative weight of a specific volume of material compared to the weight of the same volume of water, usually defined at 20 °C.

Stabilizer A substance added to prevent or retard alteration of a physical state.

Sticky point The state between a fluid and a glass where a concentrated sugar matrix is sticky to the touch. Typically defined for sugars as when the viscosity is about 10^8 kPa-s.

Styrene-butadiene rubber (SBR) An elastomer found in gum base; a co-polymer of styrene and butadiene.

Sugar bloom Surface discoloration of chocolate or coating caused by moisture.

Sweatback In soft panning, the moisture migration to the surface after application of a dry charge.

Tempering The process of pre-crystallizing the cocoa butter in chocolate to obtain the desired stable polymorphic crystalline structure.

Thixotropy Time-dependent flow behavior; the decrease in apparent viscosity over time at constant shear rate.

Triacylglycerol (TAG) Also called triglyceride, a glycerol molecule with three fatty acids esterified to each carbon atom of the glycerol molecule.

Toffee In the United States, toffee (often called English toffee) is a hard candy made from sugar and butter that often includes nuts. In many other parts of the world, toffee refers to a high cook caramel.

Vacuum Any pressure less than atmospheric pressure.

Viscosity The measure of ability for a fluid to flow; for chocolate it is a rheological parameter that defines the thickness or consistency of liquid chocolate under specified conditions such as the NCA method.

Whey The liquid product separated from curds during cheese making. Mainly comprised of water, whey proteins, lactose, and minerals.

Winnow The process of separating shell from nib of cocoa beans.

Yield stress/value A rheological parameter that defines the force needed to initiate flow in liquid chocolate.

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