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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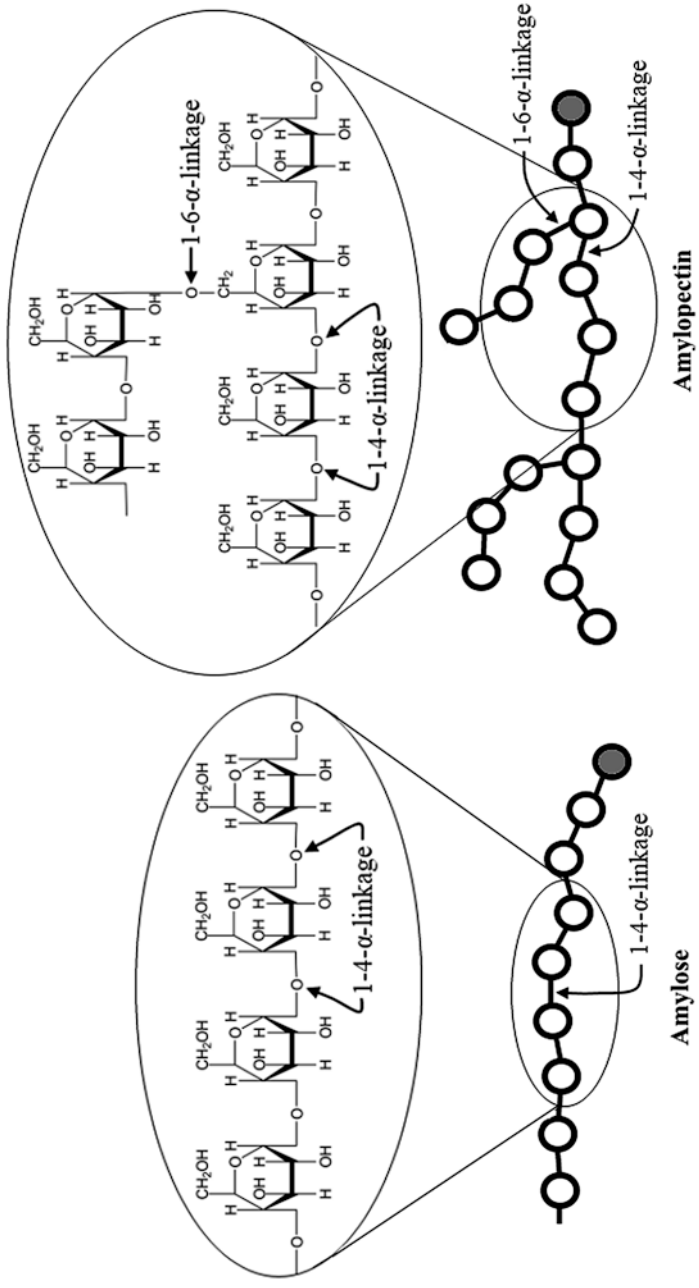


Figure 5.1 Chemical structure of amylose and amylopectin

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.

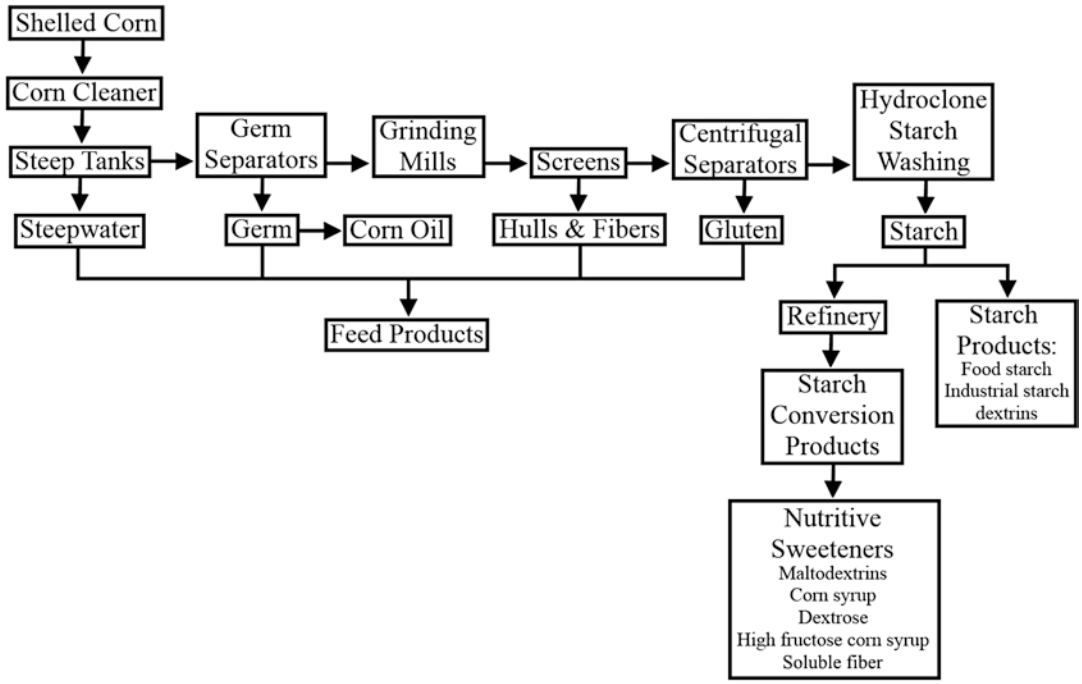


Figure 5.2 Flow chart of wet milling process to recover starch from corn

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

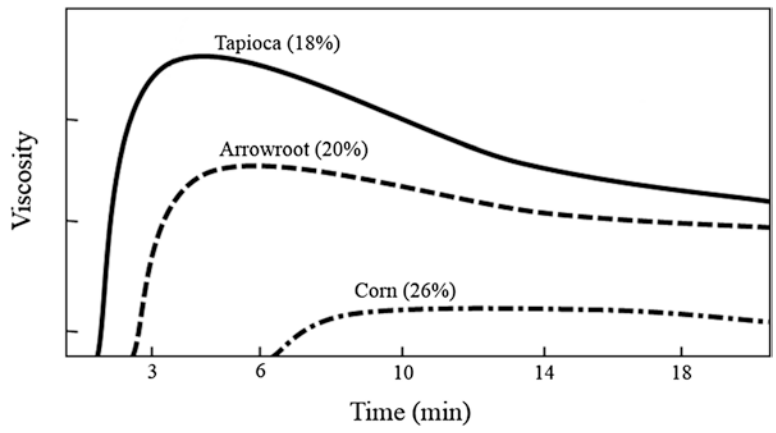


Figure 5.3 Effect of amylose content (%) in different starches on gelatinization time

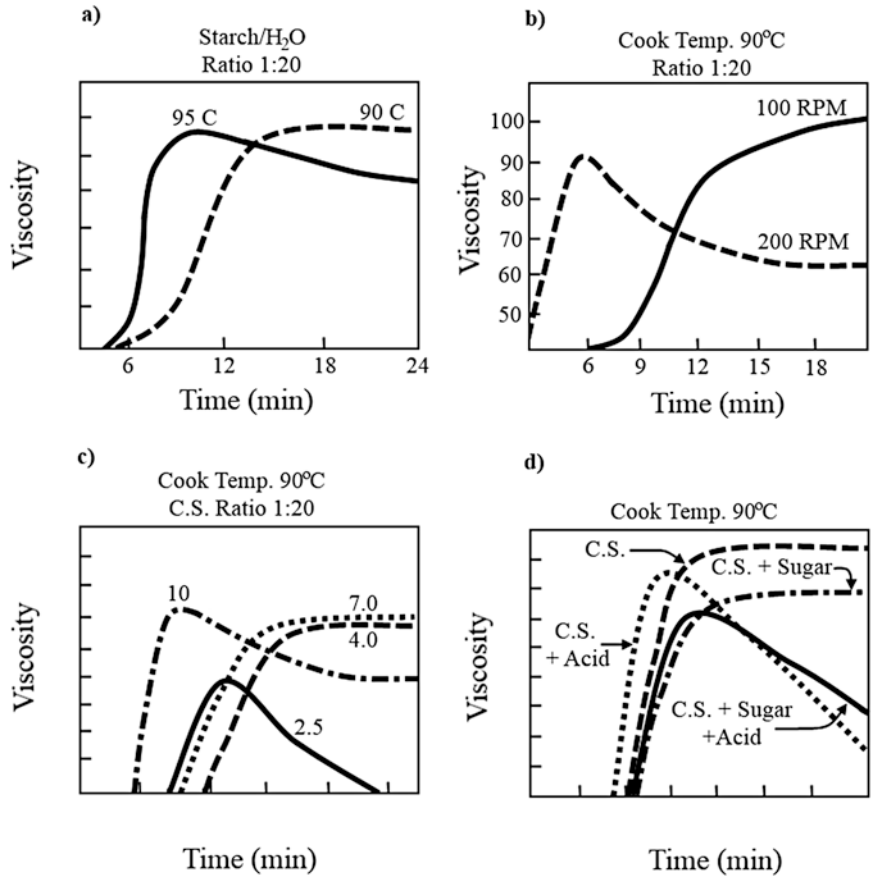


Figure 5.4 Gelatinization times of starch as affected by (**a**) temperature, (**b**) mixing speed, (**c**) pH, and (**d**) other ingredients. Starch to corn syrup (*CS*) ratio of 1:20 unless otherwise noted

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.

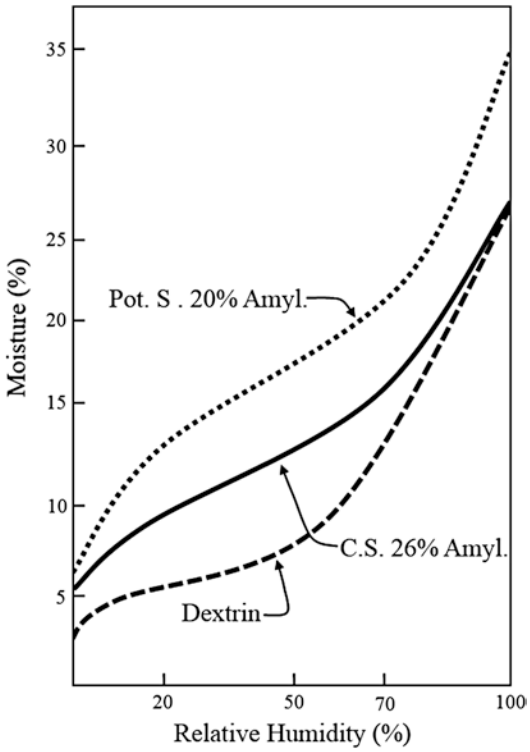


Figure 5.5 Sorption isotherms of dextrin, corn starch (*C.S.*), and potato starch (*Pot.S.*) at different relative humidities. *Amyl* amylose

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

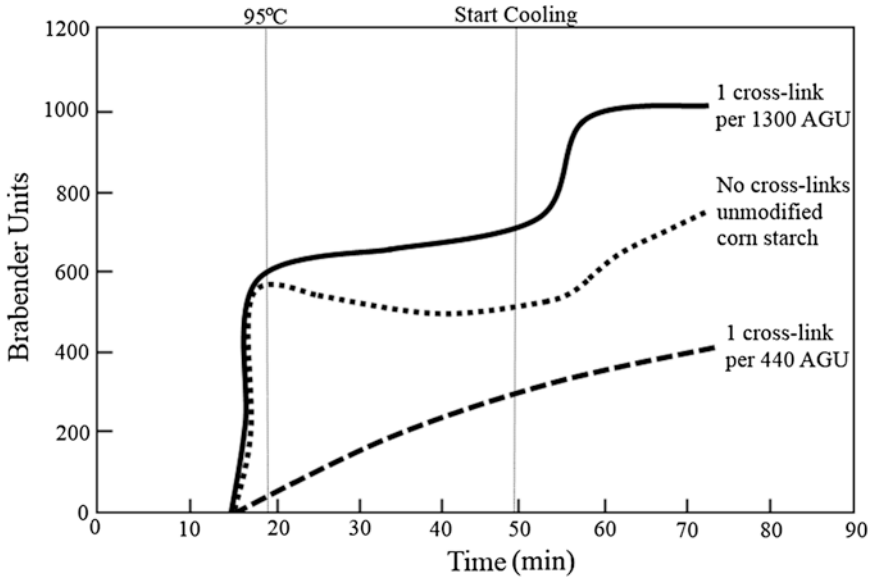


Figure 5.6 Effect of cross linking of starch on the gelatinization rate. Brabender units – arbitrary viscosity units generated by a Brabender consistometer

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.

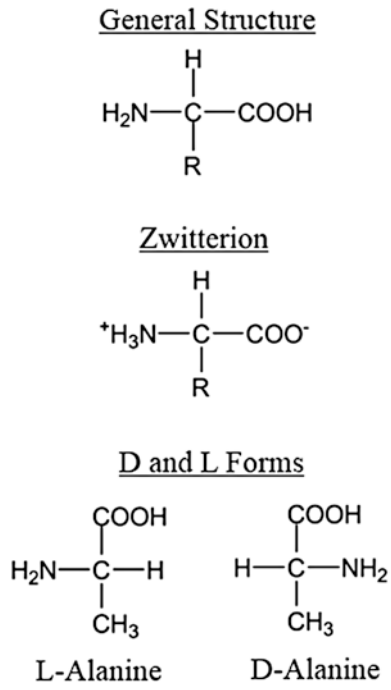


Figure 5.7 Structure of amino acids – general structure, zwitterion, D and L forms of alanine. *R* represents a carbon-based functional group, different for each amino acid

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

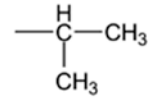
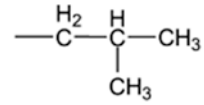
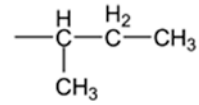
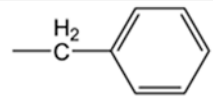
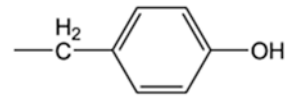
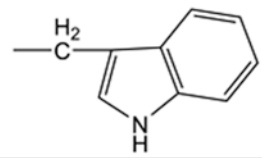
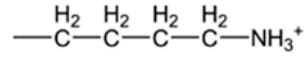
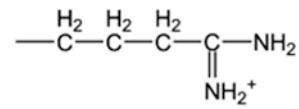
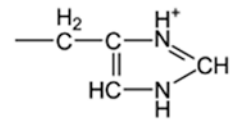
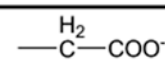
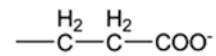
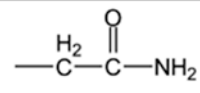
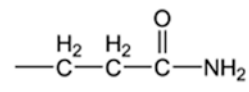
Type	Amino Acid	R-Group
"Aliphatic" Amino Acids	Glycine (Gly)	
	Alanine (Ala)	
	Valine (Val)	
	Leucine (Leu)	
	Isoleucine (Ile)	
"Aromatic" Amino Acids	Phenylalanine (Phe)	
	Tyrosine (Tyr)	
	Tryptophan (Trp)	
"Basic" Amino Acids	Lysine (Lys)	
	Arginine (Arg)	
	Histidine (His)	
"Acidic" Amino Acids	Aspartic Acid (Asp)	
	Glutamic Acid (Glu)	
"Amides"	Asparagine (Asn)	
	Glutamine (Gln)	

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

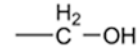
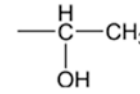
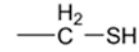
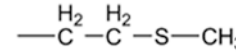
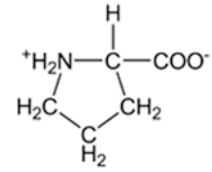
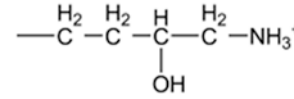
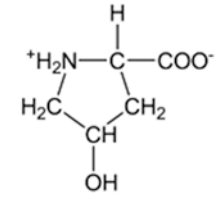
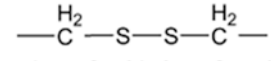
Type	Amino Acid	R-Group
"Hydroxyl" Amino Acids	Serine (Ser)	
	Threonine (Thr)	
"Sulfur" Amino Acids	Cysteine (Cys)	
	Methionine (Met)	
"Imino" Acid	Proline (Pro)	
Other Amino Acids in Proteins		
	Hydroxy-lysine	
	Hydroxy-proline	
	Cystine	 (product of oxidation of cystine)

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

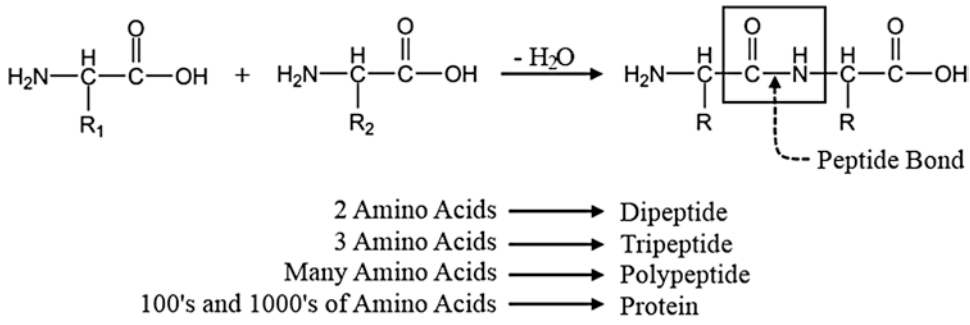


Figure 5.9 Peptide bond

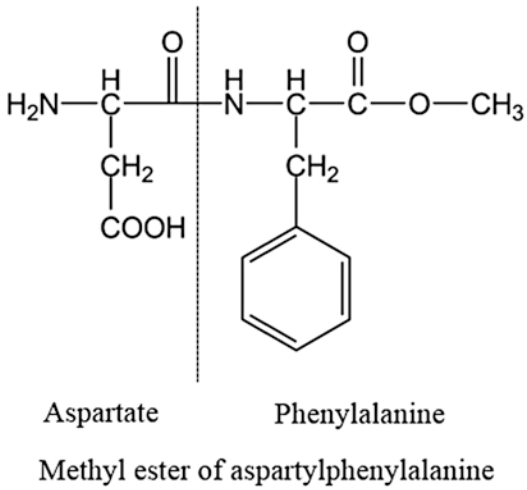


Figure 5.10 Structure of the dipeptide, aspartame

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

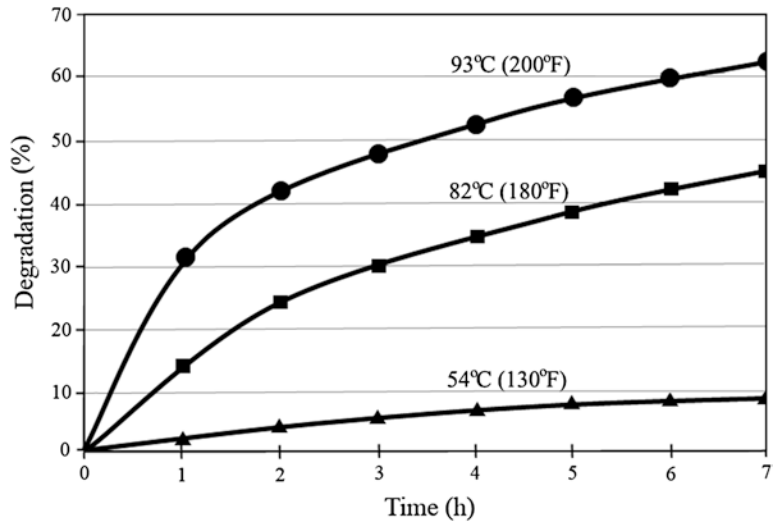


Figure 5.11 Bloom strength degradation (%) at different temperature at pH 6.0

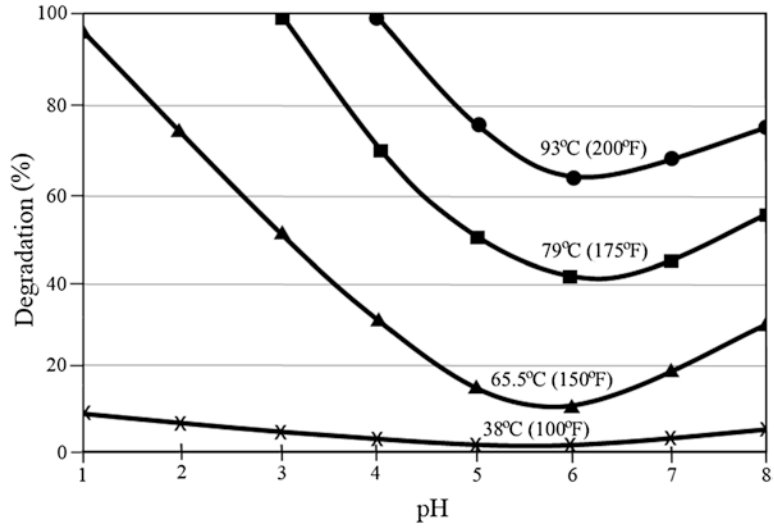


Figure 5.12 Bloom strength degradation after 7 h at different pH and temperature

(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.

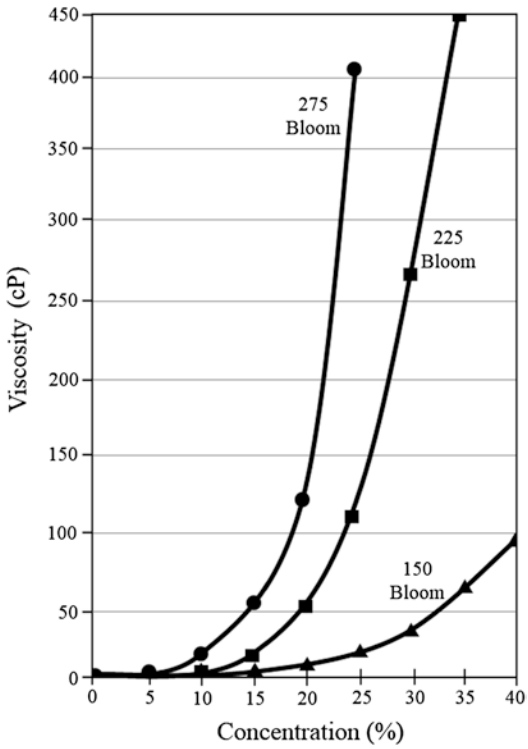


Figure 5.13 Effect of gelatin concentration on the viscosity of gelatin solutions made with different gelatin grades

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

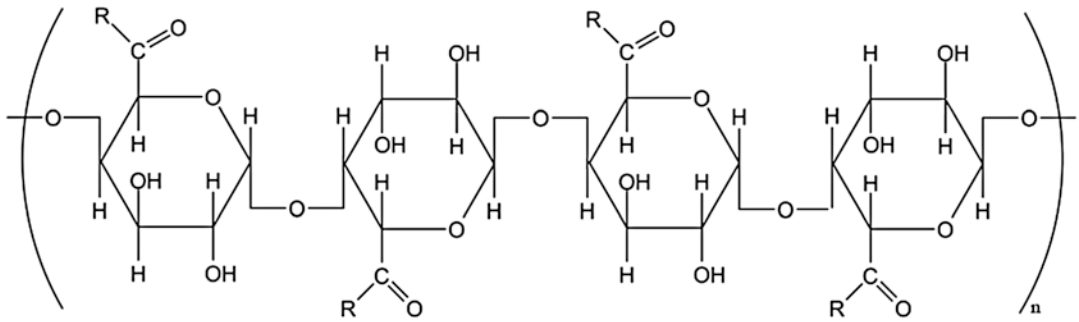


Figure 5.14 Structure of pectin. Pectic acids: R = OH; Methoxylated pectins (pectinic acids): R = OCH_3; Amidated pectins: R = ONH_2

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.

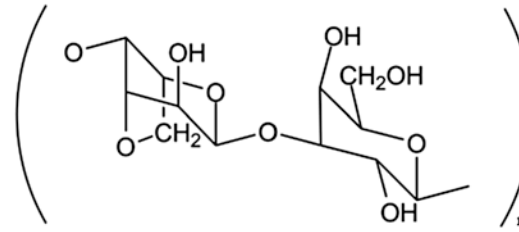


Figure 5.15 Structure of agarose

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.

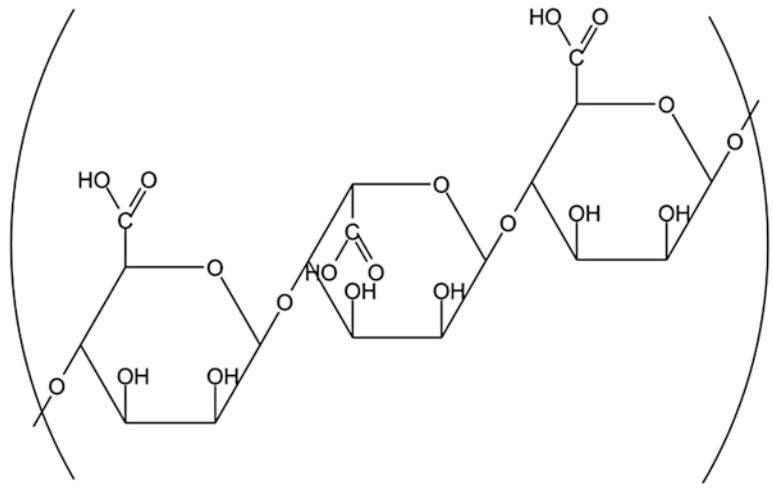


Figure 5.16 Structure of alginic acid

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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