

Chapter 1

Edible Films and Coatings: Why, What, and How?

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1.1 History and Background

Edible films and coatings, such as wax on various fruits, have been used for centuries to prevent loss of moisture and to create a shiny fruit surface for aesthetic purposes. These practices were accepted long before their associated chemistries were understood, and are still carried out in the present day. The term, edible film, has been related to food applications only in the past 50 years. One semi-sarcastic tale was that spies' instructions were written on edible films, so that in the off-chance they were captured, they could easily destroy their secrets by eating them. In most cases, the terms film and coating are used interchangeably to indicate that the surface of a food is covered by relatively thin layer of material of certain composition. However, a film is occasionally differentiated from a coating by the notion that it is a stand-alone wrapping material, whereas a coating is applied and formed directly on food surface itself. As recently as 1967, edible films had very little commercial use, and were limited mostly to wax layers on fruits. During intervening years, a significant business grew out of this concept (i.e., in 1986, there were little more than ten companies offering such products, while by 1996, numbers grew to 600 companies). Today, edible film use has expanded rapidly for retaining quality of a wide variety of foods, with total annual revenue exceeding \$100 million.¹

Why do we need edible films? Most food consumed comes directly from nature, where many of them can be eaten immediately as we take them from the tree, vine or ground. However, with increased transportation distribution systems, storage needs, and advent of ever larger supermarkets and warehouse stores, foods are not consumed just in the orchard, on the field, in the farmhouse, or close to processing facilities. It takes considerable time for a food product to reach the table of the

¹<http://www.am-fe.ift.org/cms/?pid=1000355>

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consumer. During time-consuming steps involved in handling, storage and transportation, products start to dehydrate, deteriorate, and lose appearance, flavor and nutritional value. If no special protection is provided, damage can occur within hours or days, even if this damage is not immediately visible.

As early as twelfth century, citrus fruits from Southern China were preserved for the Emperor's table by placing them in boxes, pouring molten wax over them, and sending them by caravan to the North (Hardenburg 1967). While their quality would not have been acceptable to our modern selective society, the method was quite effective for its time, and was used for centuries for lack of more efficient ones. In Europe, the process was known as "larding" – storing various fruits in wax or fats for later consumption (Contreras-Medellin and Labuza 1981). While such protection prevented water losses, the tight, thick layer interfered with natural gas exchange, and resulted in lower quality products. Larding was a compromise between maintaining moisture content and losing various qualities, including optimal taste and texture. Later in the fifteenth century, an edible film, Yuba, made from skin of boiled soy milk was used in Japan for maintaining food quality and improving appearance (Biquet and Guilbert 1986; Gennadios et al. 1993). In the nineteenth century, a US patent was issued for preservation of various meat products by gelatin (Havard and Harmony 1869). Other early preservation methods included smoking and/or keeping products cool in iceboxes or in underground cellars. Today various modern methods, including combinations of these, such as refrigeration, controlled atmosphere storage, and sterilization by both UV and gamma radiation are used to keep our food safe. Nevertheless, for many kinds of food, coating with edible film continues to be one of the most cost-effective ways to maintain their quality and safety.

1.2 Definition

1.2.1 Edible Films and Coatings

Any type of material used for enrobing (i.e., coating or wrapping) various food to extend shelf life of the product that may be eaten together with food with or without further removal is considered an edible film or coating. Edible films provide replacement and/or fortification of natural layers to prevent moisture losses, while selectively allowing for controlled exchange of important gases, such as oxygen, carbon dioxide, and ethylene, which are involved in respiration processes. A film or coating can also provide surface sterility and prevent loss of other important components. Generally, its thickness is less than 0.3 mm.

1.2.2 Generally Recommended as Safe (GRAS)

Items which are edible or are in contact with food should be generally recognized by qualified experts as being safe under conditions of its intended use, with amount applied

in accordance with good manufacturing practices. These food-safe materials must typically have approval of the Food and Drug Administration (FDA). Since it is impractical for FDA to have an all-inclusive list of every potential food ingredient, there are also other opportunities to acquire GRAS status – i.e., manufacturers can petition for approval of an ingredient or food composite provided that this petition is supported by considerable studies. There are three types of GRAS designations (1) Self-affirmed, where the manufacturer has carried out necessary work and is ready to defend GRAS status if challenged, (2) FDA pending, where results of research have been submitted to FDA for approval, and (3) No comment- which is the response of FDA if after review, it has no challenges. More detailed information on procedures to acquire such designations for industrial purposes can be found at the FDA website.² However, GRAS status does not guarantee complete product safety, especially for consumers who have food allergies or sensitivities, such as lactose intolerance (milk) and Celiac disease (wheat gluten).

1.2.3 Shelf Life

The time period, whereby a product is not only safe to eat, but still has acceptable taste, texture and appearance after being removed from its natural environment, is defined as shelf life. For practical purposes, a period of at least 2 weeks is required for processed food to remain wholesome, allowing for packaging, transportation, distribution, and display prior to consumption.

1.2.4 Light Processing

‘Light Processing’ includes a wide variety of processes used to prepare an original product or commodity for consumption, without affecting the original, “fresh-like” quality of the product (Shewfelt 1987). Light processing includes cleaning, washing, paring, coring, and dicing, for fruits and vegetables specifically, and may also include removing waste and undesirable parts from a wide variety of food products (such as de-boning of meat, etc). Although these steps are relatively unobtrusive, nature and rate of respiration changes immediately after most light processing, with the product becoming immediately more perishable. In most cases, these processes cause disruption of cell tissues and breakdown of cell membranes, creating many membrane-related problems (Davies 1987).

1.2.5 Respiration

Any type of food, whether in its natural environment or otherwise, continuously undergoes various biochemical/biological/physiological processes, which use up

²<http://www.cfsan.fda.gov/~dms/grasguid.html>

and/or release oxygen and carbon dioxide (colloquially labeled “breathing”). Depending on oxygen level, respiration can be aerobic or anaerobic. Respiration activity of a product is influenced by storage temperature, type of processing, oxygen to carbon dioxide ratio, and absolute value of oxygen concentration itself. If a wax layer is applied, oxygen content of the internal atmosphere will decrease as a function of thickness of the layer, while carbon dioxide content and anaerobic respiration will rise (Eaks and Ludi 1960). As a rule of thumb, when oxygen level drops below 3%, anaerobic respiration will start replacing the Krebs cycle, with the resulting glycolytic pathway releasing unacceptable flavors and causing other problems, such as changes in color and texture. High oxygen levels (>8%) and low carbon dioxide levels (<5%) can prevent or delay senescence in horticultural products, thus maintaining food quality (Kader 1986).

1.2.6 Transpiration

In addition to gases, food products may contain various liquid or solid components; water is most prevalent, but oils, various flavor components, and nutrients are also present. Depending on environment, these components will migrate out of or throughout the product if there is concentration difference acting as a driving force.

1.2.7 Controlled and Modified Atmosphere Storage

In order to control respiration (i.e., transfer of various gases in and out of the product), food can be stored in an environment filled with various gases at appropriate, optimal temperatures. The right gas combination can slow respiratory metabolism, and delay compositional changes in color, flavor and texture. It can also inhibit or delay microbial growth. However, this method can be quite expensive in other than large-scale stationary storage, i.e. controlled atmosphere situations. Modified atmosphere packaging (MAP) is where product is enclosed in a sealed box or bag filled with required atmosphere. Temperature, however, is critical and must be maintained at constant level to avoid in-pack condensation leading to spoilage.

1.3 Effect of Edible Films and Coatings or the Lack Thereof

Today, the most widely used commercial method for long-range protection is interim storage at low temperature (4–8°C), especially for lightly-processed food. Lowering temperature generally decreases undesirable enzyme activities, although temperature decreases down to 0–5°C may actually lead to increases in respiration rate and ethylene production (Eaks 1980). Below 0°C, growth of mold is inhibited,

but even this low temperature does not fully eliminate undesirable chemical and physicochemical reactions (Fennema 1993). For example, fruits and vegetables native to tropical climates experience harmful chilling effects such as damage to cell membranes at temperatures of 10–12°C. In addition, some cold-tolerant pathogenic microorganisms are able to grow even under refrigeration.

Accordingly, an increasing amount of research has been conducted over the past 50 years to encase a food product, such that rates of migration of molecules involved in degradative processes are maintained at natural levels and/or minimized.

Edible films are being used for a variety of purposes within a multitude of food systems, even though this fact might not be fully realized by consumers. The shiny surface of an apple in a supermarket is not provided by nature. Some candies (e.g., M&Ms) are coated with shellac to increase product shelf life and provide desired glaze. Medicine pills are often coated to prevent crumbling, to hide any bitter or undesirable taste before swallowing, and to provide controllable timed-release of medications. Even French fries are frequently coated to provide protection during cold storage before frying, control of water losses during frying, and stability against wilting and/or loss of crispness under infrared lamps between frying and serving. Edible films may also be used to limit uptake of oil and fat during frying processes (Feeney et al., 1992; Polanski, 1993). Table 1.1. provides an informative, and non-comprehensive list of examples of commercial edible coatings.

Most fresh fruits and vegetables contain considerable percentage of water, the amount of which is maintained during production in their natural environment. Respiration is maintained naturally at an appropriate equilibrium between oxygen, carbon dioxide and water by skin, which controls transmission to and from surrounding environment. However, as soon as fruits and vegetables are separated from their native production environment (i.e., harvested), the delicate balance is upset. Water activity (a_w) will change, and various physiological reactions, which were previously kept under control in developing fruit or vegetable, will accelerate

Table 1.1 List of commercially used coatings

Name	Main component	Uses
Freshseal™	Sucrose esters	Extending shelf life of melon
Fry Shield™	Calcium pectinate	Reduces fat uptake during frying fish, potatoes, and other vegetables
Nature Seal™	Calcium ascorbate	Apples, avocado, carrot, and other vegetables
Nutrasave™	<i>N,O</i> -Carboxymethyl chitosan	Reduces loss of water in avocado, retains firmness
Opta Glaze™	Wheat gluten	Replaces raw egg based coating to prevent microbial growth
Seal gum, Spray gum™	Calcium acetate	Prevents darkening of potato during frying
Semperfresh™	Sucrose esters	Protect pome fruits from losing water and discoloration
Z*Coat™	Corn protein	Extends shelf-life of nut meats, pecan, and chocolate covered peanut

post-harvest. Respiration will be affected, resulting in altered ratios of oxygen and carbon dioxide. Increased ethylene formation will accelerate ripening, thus changing color, flavor, texture and nutritional characteristics of the fruit or vegetable (Wong et al. 1994a).

Some protection against undesired changes can be obtained using controlled atmospheres and low temperatures during transportation and storage. Controlled atmosphere with high relative humidity can prevent loss of water and, with maintenance of appropriate carbon dioxide and oxygen concentrations, slow down senescence. However, with all attempts to optimize storage through controlled environments, they are still no match for Mother Nature's quality control in the field. Various undesirable changes can still occur once food has been picked and processed, and aging begins. More importantly, cost of maintaining controlled-storage environments can be very prohibitive.

These problems are not limited to just fruits and vegetables. Quality of various other food products, such as meat, pies and confectionery can also suffer before reaching the consumer. Major difficulties are deterioration of vital food components including flavor chemicals, lipids, and vitamins through oxidation. The patent issued in the nineteenth century to coat meat with gelatin to delay microbe formation and loss of water was just the beginning (Havard and Harmony 1869). Numerous research studies were carried out with reasonable success, paving the way for possible commercial applications. Loss of water which affects juiciness of meat products, was reduced by coating meat surfaces with polysaccharides to maintain desired moisture levels (Allen et al. 1963; Shaw et al. 1980). Microbes that contaminate meat can cause serious health safety problems, which can be mediated to some extent by edible films and coatings. Alginate coatings have been shown to prevent microbial growth on beef, pork, lamb and poultry (Lazarus et al. 1976; Williams et al. 1978). When frying battered or breaded meat products, too much oil may be adsorbed if batter does not adhere adequately to meat surface. By coating meat first with cellulose derivatives, oil uptake is considerably lessened (Feeney et al. 1992; Polanski 1993). Infusion of oil into chocolate presents quality problems in confectionaries, i.e., stickiness, moisture absorption, and oxidation (Paulinka 1986; Nelson and Fennema 1991). Similarly, some foods have to be protected against moisture uptake that can otherwise result in loss of crispness. Hydration of certain snack foods can be prevented by coating with sucrose fatty acid esters (Kester et al. 1990), and dried fruit can have longer shelf life when coated with zein (Cosler 1957). In case of chewing gums, an edible film is needed to prevent loss of moisture (Meyers 1994).

Uncontrolled migration of water is generally recognized as the biggest food storage/transportation challenge. Both loss and gain of water are almost always considered undesirable. Even if water loss does not cause immediate visible shrinkage to a food product, it results in economic loss via weight loss. Figure 1.1 shows that even a whole unwaxed apple will show 0.5% of weight loss after 1 day, a loss that will increase more than ten-fold when the fruit is cut in half.

On the other hand, storage in high relative humidity environments may result in water infusion causing variations in the food product between point of preparation

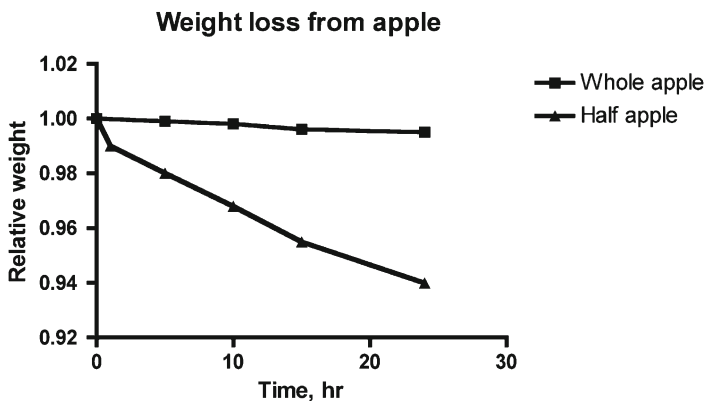


Fig. 1.1 Comparative loss of weight for whole and half apple samples

and sale. This occurrence can be a problem when regulations mandate a minimum solids content. In heterogeneous foods, if various components have different water activities, water transmission during storage can also occur internally between components of the food, causing changes to sensory characteristics. For example, moisture content between the dough and toppings of a pizza are different. If the pizza is not baked immediately after assembly, internal water migration may occur, and the original optimal moisture content of the dough will change. This change will result in different a texture of the baked product. Refrigerated storage is applied to prevent quality and safety changes in toppings (cheese, meat etc.). While refrigeration slows down water migration, water can still migrate even within the frozen product, especially if stored for a long time. Application of a film in some form on surface of the dough, before placing on the toppings, can prevent water migration and retain optimum dough structure. Similar problems exist with pies, where there is need to separate moist filling from crust to prevent sogginess (Labuza 1984), or in chocolate covered nuts, where migration of oil from nuts may retard softening of chocolate covering upon consumption (Murray and Luft 1973; Paulinka 1986; Nelson et al. 1991).

Discoloration or enzymatic browning, caused by polyphenol oxidase, is another frequent food issue. This phenomenon does not affect weight or nutrition, and sometimes not even taste, of food, but it is unsightly and results in loss due to consumer rejection. In addition, changes in gas transition result in various other equally important detrimental characteristics. These include:

- Loss and/or change of flavor and aroma
- Aesthetically unacceptable appearance
- Changes in texture

One obvious solution is to protect food from these changes until they are ready for consumption via application of edible films, which can prevent contamination, microbial growth, and pest infestation. In addition edible films can help alleviate

quality issues during quarantines that are frequently invoked on fruits due to possible infection with insect eggs. For example, many exports are held back at ports until costly fumigation is carried out. Fruits need to be stored at 1–2°C for 14–24 days before shipping from Florida to Japan (Ismail 1989). Coatings can reduce oxygen levels within the fruit and kill larva, though this method is not always optimal and may also reduce fruit quality (Hallman et al. 1994). Since potential eggs are laid on natural skin, a better way is to remove skin and enrobe fruit with edible film.

1.4 Application and Preparation of Edible Films

Edible films can provide either clear or milky (opaque) coatings, but consumers generally prefer invisible, clear coatings. Coatings can be obtained in various ways (1) by dipping the product into, or by brushing or spraying it with solution containing film ingredients, so as to deposit the film directly on food surface (Gontard and Guilbert 1994), or (2) by creating stand alone film from solution or through thermoformation for subsequent covering of food surface.

The simplest way to apply a film is directly from solution. Depending on concentration of coating solution, the product will absorb an appropriate amount of coating material necessary to form the desired layer, which when dried, forms a protective layer at the food surface. In most cases, some plasticizer needs to be added to coating solution to keep the developing film from becoming brittle. Possible food grade plasticizers are glycerol, mannitol, sorbitol, and sucrose. If coating cracks, movement of various components will increase by orders of magnitude, resulting in mass flow instead of diffusion. Coatings should have good adhesion to rough surfaces (Hershko et al. 1996). Application of a uniform film or coating layer to cut fruit and vegetable surfaces is generally difficult. Better uniformity can be promoted by adding surfactants to solution to reduce surface tension. This strategy will also reduce the superficial a_w and in turn reduce water loss (Roth and Loncin 1984, 1985). In one standard process, carboxymethylcellulose (CMC) powder was applied to cut fruit surfaces. The CMC adsorbed moisture within pores of the surface, causing the CMC to swell, which not only prevented loss of moisture, but also provided a barrier against oxygen to prevent enzymatic discoloration (DeLong and Shepherd 1972). Coatings derived from non-aqueous media, such as applying an alcohol solution of shellac to candy, result in another level of complexity. For safety reasons the finished coating layer should not contain any solvent residue. Thus, during large scale operation, disposal of exhaust gases may present environmental challenges.

Should a free-standing film be required, it can be prepared from solution by evaporation. It should be pointed out that characteristics of stand-alone films might differ from those of films created on food surfaces (i.e., those produced by dipping in or spraying). Films obtained through evaporation were found to have lower water vapor permeability than those prepared by spraying (Pickard et al. 1972). Varying rate and temperature of evaporation may result in creation of films with differing

characteristics. For example, polymer chains may be prematurely immobilized before reaching their optimal structure (by accelerated drying) to affect permeability (Reading and Spring 1984; Greener 1992). When zein films were obtained from solution after drying at 51°C for 10 min, plasticizer was needed to obtain a non-brittle material (Kanig and Goodman 1962). In contrast, drying at 35°C for 24 h yielded flexible zein films without addition of plasticizer (Guilbert 1986, 1988). Films can also be formed by cooling concentrated solutions. However rate of cooling can again result in amorphous, crystalline, or polymorphic films with differing permeabilities. The characteristics of a polymorphic film may be further modified by tempering (Landman et al. 1960; Kester and Fennema 1989a, b). Formation of flexible and stretchable films was also reported from molten acetylated monoglyceride (Feuge et al. 1953). Other possibilities are through precipitation, either by addition of selective miscible solvents that are not a solvent for the film component, or by desalting. In addition, some protein films can form upon heating, causing unfolding of polymeric chains and replacement of intramolecular with intermolecular bonds. This transition affects permeability. In case of proteins, improved films can be obtained by adjusting coating solution pH in relation to the protein isoelectric point, where proteins become least soluble. However, this process does not necessarily improve resistance of films to water transmission (Krochta et al. 1988). The pH can be also adjusted by high pressure liquefied carbon dioxide treatment which although costly, does not leave any salt residue (Tomasul et al. 1997).

When films, comprised of pectin or alginate, are prepared by evaporation from water-soluble components, they are subject to re-dissolution in water or destruction in high humidity conditions. This problem can be avoided by cross-linking polymers at the film surface. Various reactions can be employed to achieve enhanced covalent bonding (e.g., treatment with formaldehyde); however such reactions can create new chemical structures that might necessitate approval by FDA. The most acceptable cross-linking method involves ionic interaction between polymer chains via multivalent ions to form ionomers. While most synthetic films have higher tensile strength than typical edible films, ionomers are exceptions (Pavlath et al. 1999a; Pavlath et al. 1999b). For ionomers, tensile strength of their films is dependent on number of available bonding locations. Ionomer cross-linked films can be used as wrapping materials or, in case of water solubility, as bags that dissolve when immersed in water during food preparation (e.g., soup). In such cases, films do not have to be thin, because they will disappear before tasting and can further act as thickening agents within the food product. This aspect is especially important from an environmental perspective, where disposal is not necessary (becomes consumed as part of the food). Commercial synthetic materials are not generally biodegradable, while edible films typically are. Thus, edible films provide an ideal solution for minimizing packaging waste onboard ships during long voyages, during which maritime regulations forbid throwing of any refuse overboard. While most synthetic commercial packages possess average life times of 200 years in a marine environment, edible films decompose readily providing an environmentally-friendly solution.

Thermoformation is rarely used to create edible films, because most edible components cannot be molded at elevated temperatures without causing irreversible

structural changes to the material. Hydroxypropylmethylcellulose and polylactic acid, two biodegradable thermoplastics, are rare exceptions. Any protein-containing cysteine, such as gluten, hair or chicken feather, represents interesting thermoplastic biomaterials, depending on level of cysteine content. When these materials are treated with reducing agents, such as sodium sulfite, disulfide bonds can be cleaved at 90–100°C. This bond cleavage lowers protein molecular weight allowing the material to flow under slight pressure without decomposition. The reduced disulfide bonds can then easily reform resulting in a strong, pliable material (Pallos et al. 2006). Disulfide bonds in some of these proteins are also susceptible to reduction in appropriate solvents with disulfide bridges reformed during solvent evaporation (Beckwith and Wall 1966; Okamoto 1978; Gennadios et al. 1993). As protein molecules undergo unfolding upon heating, new or non-native disulfide bonds may also form to enhance intermolecular cross-linking (Schofield et al. 1983). It was reported that preparation of such films under acidic conditions provided better quality films than under alkaline conditions (Gontard et al. 1992).

Packaging issues are further complicated by strong demand for convenience foods. With fast moving lifestyles of today, consumers desire to spend less time in the kitchen preparing meals. True, an apple can be eaten as a whole fruit but to use it in an apple pie or fruit cocktail, non-edible and/or unappetizing parts of the fruit need to be removed. Consumers do not generally want to waste time with so-called light processing of foods (i.e., skinning and pitting fruits, slicing vegetables, skinning chickens, or just cleaning food surfaces). At the same time, consumers expect appetizing appearance and mouthwatering flavor.

Preparation processes can be tedious and time-consuming. In small-scale commercial operations, such as cafeterias, automatic processing machines can now do much of the light processing work, but cost of such machinery is still too high for typical home kitchens. On the other hand, large-scale commercial processing in a centrally-located factory provides both economical and environmental benefits. In this setting, energy costs are minimized by scale of operation, disposal and/or utilization of waste is carried out efficiently at centralized locations, and volume (cost) benefits are achieved. However, removal of a food from its natural state and environment also accelerates undesirable changes that can lead to deterioration of appearance, texture, and taste. We have all likely had the experience of biting into an apple, setting it down for a few minutes, and then observing how quickly the exposed surface has turned brown. Extensive browning is apparent on apple slices within 30 min, though surface discoloration begins to occur even after just a few minutes (Bolin et al. 1964).

What is the cause of these changes? Natural skin does not hermetically seal fruit from its surroundings. Rather it maintains optimal gas exchange equilibrium to protect against weight loss, discoloration, loss of flavor and texture, among other attributes. While such products are still subject to various aerobic and anaerobic respiratory processes, these processes are maintained in proper balance by natural skin. However, when fruit or vegetable is cut or even just mechanically damaged, cell wall membranes are disrupted, initiating a cascade of various enzymatic processes. Even minimal mechanical damage incurred during handling and transport

can stimulate increased formation of ethylene causing physiological disorders and deterioration (i.e., increased cell permeability, loss of compartmentalization, and increased enzyme activities) (Hyodo et al. 1978). Change in the rate of migration of oxygen, carbon dioxide, and ethylene can result in anaerobic fermentation and increased ripening. Even the way in which fruits are cut can make a difference. For example, formation of a white, unappetizing layer on carrot surfaces can be prevented by peeling them with a sharp blade (Bolin and Huxsoll 1991). Water knife cutting can also decrease slicing-related issues (Becker and Gray 1992). Cut surfaces increase chances for growth of microorganisms, causing multiple-fold increase in respiration (Maxcy 1982). Increased respiration rates open up possibilities for cascading biochemical changes, such as degradation of carbohydrates, activation of dormant biological pathways, and facilitation of new, additional enzymatic activities (Uritani and Asahi, 1980) which may induce production of unusual metabolites (Haard and Cody 1978; Griesbach 1987). This circumstance occurs with polyphenol oxidase, an enzyme associated with catalysis of browning in fresh fruits and vegetables, via rapid oxidation of *o*-quinones and polymerization of oxidized products to melanin (reddish-brown in color).

Nature generally maintains optimum level of water activity (a_w) in most fruit and vegetable products. Conversely, if addition of a protective edible film unduly restricts water migration, resulting increase in water activity may cause undesirable changes. The most frequent problem is growth of microorganisms, such as mold and yeast. Biochemical and enzymatic reactions may also be induced by increasing water activity affecting taste, appearance and crispness. On the other hand, increasing water content can plasticize cellular structure, leading to loss of crispness in some products, as well as increased permeability. Table 1.2, summarizes effect of water activity (a_w) levels as they relates to various undesirable changes associated with fresh fruits and vegetables. For non-enzymatic browning the rate increases until water activity reaches 0.6 and then declines (Rockland and Nishi 1980).

Many food storage issues can be minimized by dehydration or lowering of moisture content of a food product. Unfortunately normal food dehydration procedures may also remove many of the volatile flavor components, which are not restored upon simple rehydration. Interestingly if a food product is coated and then dehydrated osmotically at room temperature (the OSMEM process), only water is removed from the product. This process uses thicker films (1.5–2.0 mm thickness) which, if water soluble will dissolve during rehydration process (Camirand et al. 1968, 1992).

Table 1.2 Quality problems associated with changes in water activity

Water activity	Quality problem	Reference
0.2	Non-enzymatic browning	Labuza (1980)
0.4	Loss of crispness	Katz and Labuza (1981)
0.6	Mold formation	Troller (1980)
0.7	Yeast formation	Troller (1980)
0.8	Bacterial growth	Troller (1980)

1.5 Migration Processes

Several important parameters need to be defined to describe diffusion processes in relation to films. Migration between two adjacent volumes separated by a layer or membrane, occurs in three basic steps. In the first step, the diffusing molecule comes in contact with surface of the layer or membrane, and is adsorbed onto it. In the second step, the molecule then diffuses through the thickness of the layer or membrane. Lastly, once the diffusing molecule reaches the other side of the layer or membrane, it will desorb. Rate of adsorption and desorption is dependent on the affinity between the diffusing molecule and membrane (film) components, especially for water migration. Hydrophilic materials rapidly adsorb water but rate of desorption on the opposite side of the membrane will be controlled by partial pressure of water in that volume.

Despite surface effects noted previously, the most dominant factor in molecular migration is bulk effect – rate of diffusion of molecules while in the membrane or film. In an ideal case, amount of given material (Q) passing through a film can be determined by Fick's law of diffusion (1.1):

$$Q = PA\Delta p t / d, \quad (1.1)$$

where Q increases in direct proportion to film surface area (A), and decreases with its increasing thickness (d). Increasing partial pressure difference (Δp) of migrating molecule between two sides of the membrane and time (t) also linearly affects total amount of permeate. Permeability coefficient (P) is defined as the product of diffusion coefficient (D) and solubility (S) coefficients ($P = DS$). In an ideal case, P is a constant determined by characteristics and structure of the film.

When a given product is encased in protective film, the outer surface conditions are already given. Ability to maintain low partial pressure difference (for a given component) between the inside of the food product and surrounding external environment is generally limited by economic factors (requires a controlled atmosphere). When a coated product is stored openly in a relatively large area, amount of gas in the surrounding external environment is orders of magnitude higher than amount that is diffused out from the product. If the coated product is placed within an enclosed system (e.g., in a bag or box), equilibrium can be created between the product and surrounding external environment, depending on head-space volume relative to product weight. Film thickness is another important factor in the rate of water and gas transmission, changing not only appearance, but also taste of a food product. While an increasing film thickness will slow down rate of diffusion, there is also a practical limit to consider. If protective coating is edible and is to be ingested together with the product, it must be applied in minimal fashion so that it will not adversely modify original product taste. An exception can be made if a flavor change is considered to be acceptable or product is baked after coating (generally nullifies most additive flavors) or dissolved before being consumed. Therefore, diffusion is mostly dependent on size of the permeate molecule and abundance of "holes" or "channels" in the film molecular structure, through which

the permeate can move. Solubility coefficient is influenced by the permeate's ease of condensation and its affinity to components of the film.

In the earlier form of Fick's law (1.1), it was assumed that temperature is constant. Effect of temperature on permeability constant follows Arrhenius law (1.2):

$$P = DS = D_0 S_0 / \text{Exp}((E_{ad} + \Delta H_s) / RT), \quad (1.2)$$

where D_0 and S_0 are reference values for diffusivity and solubility, E_{ad} is activation energy of diffusion, and ΔH_s is enthalpy of sorption. Since E_{ad} is positive, diffusion increases with increasing temperature. However, since ΔH_s is negative for water, solubility decreases at the same time (Rogers 1985). In hydrophobic films, it was found that water vapor permeability increased with increasing temperature indicating that the controlling factor is diffusion (Hagenmaier and Shaw 1991). Some anomaly was observed with the water vapor transfer rate, which decreased with decreasing temperature over range of 40–20°C, indicating greater absorption. However, water vapor transfer rate remained constant between 20 and 10°C, and permeability increased at 4°C (Kester and Fennema 1989c).

A film or coating must be fairly uniform and free of pinholes, microscopic cracks, and rough surfaces. Therefore preparation conditions (e.g., rate of evaporation and temperature) are important factors in film preparation. Even a small degree of irregularity in a film can exponentially increase rate of diffusion, which is not accounted for by Fick's law. However, rate of diffusion is indirectly proportional to square root of molecular weight of the diffusing molecule; therefore it is a relatively smaller problem for oil, flavor, and other similarly large molecules (relative to water, oxygen, carbon dioxide and ethylene). In the molecular weight range of the most important gases (oxygen, carbon dioxide, water and ethylene), diffusion rate due to film irregularity is by orders of magnitudes faster than that which occurs through the film structure itself. When one pinhole, representing only 0.008% of film surface, was intentionally made, water vapor transmission increased 2.7 times (Kemper and Fennema 1984).

It is evident that Fick's law has additional limitations, especially for cases in which the film includes hydrophilic polymer components. Relative humidity and temperature may alter considerably the diffusion and solubility coefficients of film components (Gontard et al. 1996). At high relative humidity, water uptake can soften film structure through plasticization, making it easier for diffusing molecules to pass through the film. Solubility coefficient of film components also increases (Cairns et al. 1974). Another anomaly, shown by various authors (Landman et al. 1960; Biquet and Labuza 1988; Martin-Polo et al. 1992), concerns influence of thickness of film on water vapor transfer. In very thin films of less than 60 μm , water vapor transfer decreases according to Fick's Law; however, above this thickness level, water vapor transfer rate remains almost constant.

Value for permeability ($P = DS$) is essentially dictated by structure of the film. At the molecular level, diffusing molecules migrate through polymer chains and side chains, which are held in place by hydrogen bonds and van der Waals forces. Side chains can have either beneficial or detrimental influence on permeation coefficient

of film. In one sense, a side chain can decrease available intramolecular spacing within the film, which allows migration of permeates, thus making diffusion more difficult. On the other hand, a side chain may decrease degree of crystallinity within a film by introducing more structural irregularities. Crystallinity rigidifies polymer chains, which hinders molecular migration through a film by limiting molecular mobility of film components. Thus, crystalline packing arrangement of polymers and their orientation within a film relative to flow direction especially influence migration of molecules through a film (Fox 1958). These elements regulate “free space” within the film available for migration, and limit molecular movement from cavity to cavity.

In certain cases, protection against migration can be created at surface of a food product without addition of polymeric material. If the surface already has a polymeric structure, these surface polymers can be cross-linked, whereby the product itself provides a new protective layer. For example, this strategy was employed quite successfully for apple slices through creation of an ionomer surface using calcium ascorbate dips. In this scenario, calcium ions interacted with surface pectin molecules, closing the surface, while also incorporating ascorbic acid as an antioxidant (Pavlath et al. 1996; Chen et al. 1999). Calcium formed salt bridges between the carboxylate groups of pectin polymer chains creating cross-links that promoted a more rigid structure (the so-called egg-box model) and decreased permeability at food surface (Grant et al. 1973; Wong et al. 1996). Such treated samples did not brown or lose water over a 2 week period (Chen et al. 1999). Similar protective layers can be formed on potato strips through treatment with calcium acetate and an oxidation inhibitor. Cross-linking at surface of potato strips prevented both oxidation and discoloration, and provided for higher quality French fries upon frying (Mazza and Qi 1991).

There are various synthetic films and packaging materials available for minimizing migration, but with few exceptions, these materials are not edible and cannot be consumed together with food. Thus, they must be removed before consumption. Economics is a primary driver in the choice between use of synthetic and edible films. Edible films are relatively more expensive, with their commercial utilization being limited to convenience food items (e.g., snack foods), where consumers are willing to may pay more. Synthetic, non-edible materials are generally better suited for creating modified packaging environments, creating sealed, box-like enclosures that may be supplemented with special atmosphere. Edible film materials generally decompose more rapidly or lose their quality and integrity faster (oxidation, dissolution, etc.) than those of synthetic origin. On the other hand, synthetic packaging materials have to be removed before eating, leading to challenges in relation to disposal and environment. Many packaging materials end up as litter.

Edible encasing materials must meet standards first, by ensuring that they are labeled GRAS for consumption by the Food and Drug Administration. Secondly, consumers are very selective and finicky in relation to what they choose to eat. Unless different a flavor or texture is intended to enhance consumer acceptance, the film or encasing should not adversely change taste and flavor of the food product, and should also be invisible and undetectable to taste. What materials can then be used to fulfill these difficult requirements?

1.6 Possible Components of Edible Films

The main components of our everyday foods (e.g., proteins, carbohydrates and lipids) can fulfill requirements for preparation of edible films. As a general rule, fats are used to reduce water transmission; polysaccharides are used to control oxygen and other gas transmission, while protein films provide mechanical stability. These materials can be utilized individually or as mixed composite blends to form films provided that they do not adversely alter food flavor. A major objective in preparing films for many foods (e.g., fresh fruit and vegetables) is to ensure that the generated films afford physical and chemical properties necessary to maintain transmission of various gases and liquids at the same rates as they occur within their native systems. Chemical structures of the three major components used to prepare films differ widely, and therefore attributes that each component contributes to overall film properties are different too. The following is a short informative summary of these concepts.

Films from various sources of protein, such as corn, milk, soy, wheat and whey, have been used for years, their major advantage being their physical stability. It should be mentioned, however, that most of these protein sources are in fact mixtures of various proteins comprising a range of molecular weights. If they are used in solution rather than in emulsion, the solution will contain different protein fractions than the emulsion (unless all protein fractions are equally dissolved). Lower molecular weight components are generally more easily solubilized, though they exhibit higher permeabilities than higher molecular weight entities within films. While this limitation can be counteracted with cross-linking, edibility and mouthfeel of a film can be jeopardized by such treatment. When selecting protein for use in an edible film, consideration should extend beyond just protein functionality and GRAS status. It is important to recognize that a given segment of population is allergic to certain proteins, specifically to those of wheat. Consequently, collagen can be extruded to desired shapes such as a casing for sausage links. Collagen replaced traditional casing material (derived from animal intestines) because of its ease of manufacture and scale-up. In general, value of proteins as moisture barriers is low, and they also do not adequately control transfer of oxygen, carbon dioxide and other gases that are important to stability of various foods. Their major advantage is their structural stability, which makes it possible to hold a required form (e.g., sausage casing). Cross-linking can also occur in proteins where the isoelectric point is dependent on interaction of the amino and carboxylic groups of the protein. Thus depending on protein composition, permeability can also be altered. It was reported that depending on the pH of solution from which the film was cast, properties (e.g., color, texture, tensile strength) were markedly different (Gennadios et al. 1993; Gontard et al. 1992.)

Water adsorption occurs readily at surface of polysaccharide films (e.g., those of alginate, carrageenan, cellulose and its derivatives, dextrin, pectin and starch), because of the hydrophilic nature of most polysaccharides. Some polysaccharides such as cellulose derivatives, have lower water transmission than average polysaccharides, though they are still less effective than wax. The primary advantages of

polysaccharide films are their structural stability and ability to slow down oxygen transmission. As a general rule films which do not provide protection against water transmission often have desirable properties in preventing oxygen transmission and vice versa (Banker 1966). Resistance to gas transmission can be so effective for polysaccharide films that it can be a challenge to manipulate. For example, permeability for oxygen in high amylose starch films was found to be virtually zero despite addition of plasticizers that were known to increase gas permeability (Mark et al. 1966). Therefore, in spite of their shortcomings with regard to water permeability, polysaccharides can be used to protect food from oxidation. Alginate coating can prevent lipid oxidation and stop rancidity (Mate et al. 1996). Another interesting role of polysaccharide films is to act as "a sacrificing agent" instead of as a barrier. Since most polysaccharides and other hydrophilic materials provide low protection against water transmission (i.e., they are highly hygroscopic), they may be applied as relatively thick films at food surfaces to intentionally absorb water and provide temporary protection against further moisture loss (similar to how a surfer's wet suit takes in water, but provides protection). Carrageenan, a sulfated polysaccharide of D-galactopyranosyl units was found to form a structured gel, which acted as sacrificing agent (Glicksman 1982, 1983). Alginate gels were also reported to possess this function (Shaw et al. 1980). Thus the coated product itself does not lose significant moisture until the sacrificing agent or film itself is dehydrated. If a surfactant is added to the coating, surface water activity can be altered without altering water content inside.

Waxes and fats are the oldest known edible film components. While most waxes are of natural origin, synthetic acetylated monoglycerides have similar characteristics and have been used with the blessing of the FDA in edible films for meat, fish and poultry. Originally, lipid coatings were applied by simply pouring molten paraffin or wax over citrus fruits. This process slowly gave way to adding a thin shiny layer by applying small amount of various wax through dipping or spraying. The hydrophobic fruit surface, which also protects against abrasion during transportation, adds an aesthetic appearance. At the same time, thin wax coatings still allow some breathing to occur. They are excellent barriers to water transmission, while still slowing or altogether preventing other gas migration. Wax will affect oxygen and carbon dioxide transmission, and thus, can result in unwanted physiological processes, such as anaerobic respiration. This process in turn, will diminish quality of the product, resulting in softening of tissue structure, alteration of flavor, delay of ripening, and promotion of microbiological reactions (Eaks et al. 1960). In case of horticultural products with minimal respiration such as root vegetables, thick layers of wax are less harmful and can be used (Hardenburg 1967). It was reported that water vapor transmission through fatty acid monolayers decreased logarithmically as length of the fatty acid hydrocarbon chain increased, though this effect was not indefinite (LaMer et al. 1964). However, there is disagreement about the most efficient chain length. According to one group, the most efficient chain length is C_{12} - C_{14} (Wong et al. 1992; Pavlath et al. 1993; Talbot 1994), while another group found that chain lengths of C_{16} - C_{18} (Hagenmaier and Shaw 1990; Koelsch and Labuza 1992; McHugh and Krochta 1994; Park et al. 1994) gave best results.

However, introduction of double bonds into the chain increases water vapor transmission 80-fold (Roth and Loncin 1985; Hagenmaier and Baker 1997), which is attributed to loss of crystallinity.

Application of edible films is especially difficult when applying lipophilic material to wet surfaces, such as cut fruits and vegetables. Direct application of any lipid to a hydrophilic or wet surface results in weak adhesion at the film-food interface. Dual-coating is one possible solution to this problem, as it provides protection against more than one permeate through use of different laminate layers. For example, the wet cut surface of an apple was first coated with alginate cross-linked via calcium ions. This initial coating provided a more appropriate foundation for subsequent hydrophobic coating with acetylated monoglyceride (Wong et al. 1994a). Unfortunately, two coating processes increase product cost and may also reduce commercial viability. Emulsions represent another approach to apply film, although it is still not clear whether emulsion-cast films are better than dual-coatings. Two conflicting reports, each claiming multiple-fold advantages cite that emulsions are much better than dual coatings (Kamper and Fennema 1984) and vice versa (Martin-Polo et al. 1992, Debeaufort et al. 1993). A more recent study forwards the general belief that multilayer films provide better protection than single layer films from emulsions (Debeaufort et al. 1998).

From an economic point of view, emulsion-cast films have commercial appeal for several reasons. Use of a mixture of fat and carbohydrate components emulsified by protein, allows for direct adhesion of hydrophilic carbohydrate material at food surface and formation of a hydrophobic layer or coating at the external food surface. An aqueous emulsion containing 10% casein, 1% alginic acid and 15% of acetylated monoglyceride by weight resulted in a coating that reduced moisture losses for apple slices by 75% over a 3-day period – relative to uncoated slices. Effectiveness of this coating was unexpected, because alginic acid is hydrophilic and moisture losses should have been less if it were left out from the mixture. However, when the coating mixture did not contain either alginic acid or casein, there was only minimal decrease in water loss. It can be implied that casein provided a bridge between hydrophilic alginic acid and hydrophobic lipid, allowing adhesion to the hydrophilic cut surface (Pavlath et al. 1993; Wong et al. 1994b).

Characteristics of emulsion-derived films however, are sensitive to quality of emulsion – generally requiring droplet sizes of $<0.5 \mu\text{m}$ (Platenius 1939). In fact, droplet size should be in the 10–100 nm range to obtain an optimal thermodynamically stable microemulsion (Das and Kinsellar 1990). However, there are several drawbacks to emulsion-type coatings. These coatings can be wet and difficult to handle and may function more as a sacrificial layer as opposed to a true moisture barrier. Emulsion stability is also sensitive to temperature and its efficiency can be affected by quality of emulsifier used. Such variations represent a handicap to commercial application. One particularly interesting breakthrough that eliminates the need to emulsify polysaccharide-fat coating mixtures is use of amphiphilic compounds, molecules containing both hydrophilic and lipophilic moieties. One such example is sucrose fatty acid ester, which was efficient for retaining crispiness of a snack food (Kester et al. 1990). Casein treated with acyl esters of *N*-Hydroxysuccinimide

yielded fatty acid acylated casein with hydrophobic characteristics (Nippon 1984). Another possibility is chitosan fatty acid salts, where length of the fatty acid chain plays an important role in rate of water vapor transmission. Microstructure of these salts changes dramatically though, when lauric acid is incorporated into the chitosan film instead of shorter or longer fatty acids. Chitosan laureate had the best moisture barrier properties in comparison to both shorter and longer fatty acid chain complexes (Wong et al. 1992). The product is a composite film in which fatty acid molecules are distributed within the chitosan matrix, suggesting the importance of the morphological arrangement of the lipid within the chitosan matrix (Pavlath et al. 1993). This arrangement would have an added advantage, since both chitosan and lauric acid alone are antimicrobial agents (Kabara and Ecklund 1991; Darmadji and Izomimoto 1994). Unfortunately, chitosan is still not fully accepted in the United States for food applications, even though it is approved for use in Canada and Japan.

1.7 Conclusions

Various reviews have been written about properties and potential uses of edible films (Kester and Fennema 1986; Guilbert 1986; Krochta 1992; Krochta et al. 1994; Morillon et al. 2002). An extensive review on antimicrobial films was also published (Cagri et al. 2004), and a special review is available for applications on various types of meat products (Gennadios et al. 1997). Much more research is needed as there is no universal edible film that is applicable for every problem. Obviously, specific barrier requirements and food product specifications will determine the type of layer that is best for a given situation. Products with high moisture contents need fatty layers to prevent loss of water. To prevent possible discoloration, an oxygen barrier component is needed. Unsaturated fats which are easily oxidized require similar protective layers. As stated above, water and oxygen permeability generally are inversely related; thus, many films will need to be composite materials with multiple properties (not unlike Mother Nature's own protection). Ideal edible film should have the following characteristics:

- Contain no toxic, allergic and non-digestible components
- Provide structural stability and prevent mechanical damage during transportation, handling, and display
- Have good adhesion to surface of food to be protected providing uniform coverage
- Control water migration both in and out of protected food to maintain desired moisture content
- Provide semi-permeability to maintain internal equilibrium of gases involved in aerobic and anaerobic respiration, thus retarding senescence
- Prevent loss or uptake of components that stabilize aroma, flavor, nutritional and organoleptic characteristics necessary for consumer acceptance while not adversely altering the taste or appearance
- Provide biochemical and microbial surface stability while protecting against contamination, pest infestation, microbe proliferation, and other types of decay

- Maintain or enhance aesthetics and sensory attributes (appearance, taste etc.) of product
- Serve as carrier for desirable additives such as flavor, fragrance, coloring, nutrients, and vitamins. Incorporation of antioxidants and antimicrobial agents can be limited to the surface through use of edible films, thus minimizing cost and intrusive taste.
- Last but not least – be easily manufactured and economically viable

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