

PROTEIN-BASED FILMS and COATINGS

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Proteins as Raw Materials for Films and Coatings: Definitions, Current Status, and Opportunities

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INTRODUCTION

IN the past approximately 50 years, impressive advances have been made in the production of synthetic polymer films designed to protect foods, pharmaceuticals, and other products and to perform other functions such as mulching. With the increasing population and stress on limited resources and the environment, uses of renewable resources to produce edible and biodegradable films that can improve product quality and/or reduce waste disposal problems are being explored.

A number of reviews and books have considered the materials, properties, and potential applications for edible films and coatings (Daniels, 1973; Guilbert, 1986; Kester and Fennema, 1986; Krochta, 1992, 1997a, b, c; Lindstrom et al., 1992; Conca and Yang, 1993; Cuq et al., 1994; Koelsch, 1994; Krochta et al., 1994; Baldwin et al., 1995a, b; Callegarin et al., 1997; Gennadios et al., 1997; Myllarinen et al., 1997; Debeaufort et al., 1998; Baldwin, 1999), biodegradable films and coatings (Huang, 1985; Kuman, 1987; Huang et al., 1990; Ching et al., 1993; Satyanarayana and Chaterji, 1993; Chapman, 1994; Fishman et al., 1994; Griffin, 1994; Jane, 1994; Narayan, 1994; Gebelein and Carraher, 1995; Fuller et al., 1996; Krochta and De Mulder-Johnston, 1996; Cuq et al., 1997; Guilbert et al., 1997; Petersen et al., 1999), or both edible and biodegradable films and coatings (Gontard and Guilbert, 1994; Guilbert and Gontard, 1995; Martin-Polo, 1995; Anker, 1996;

Ahvenainen et al., 1997; Guilbert et al., 1997; Krochta and De Mulder-Johnston, 1997; Sessa and Willett, 1998; Arvanitoyannis and Gorris, 1999). Several reviews focused exclusively on either proteins (Gennadios and Weller, 1990; Gennadios et al., 1994a; McHugh and Krochta, 1994a; Torres, 1994; Krochta, 1997b; Cuq et al., 1998), polysaccharides (Nisperos-Carriedo, 1994; Nussinovitch, 1998), or lipids and resins (Hernandez, 1994; Baldwin et al., 1997; Callegarin et al., 1997; Shellhammer and Krochta, 1997a).

The main focus of this book is on protein-based films and coatings. The objective of this introductory chapter is to (1) define edible and biodegradable films and coatings and the nature of proteins used to form such structures; (2) define methods available for protein film and coating formation and the properties measured to evaluate protein films and coatings; (3) summarize the barrier, mechanical, and other properties possessed by protein-based films and coatings; and (4) discuss existing and potential applications for protein films and coatings.

DEFINITIONS, FUNCTIONS, AND RATIONALE

FILMS VERSUS COATINGS

Films are normally regarded as stand-alone, being formed separate of any eventual intended use. These stand-alone films also are used as testing structures for determination of barrier, mechanical, solubility, and other properties provided by a certain film material. Such films can be used as covers, wraps, or separation layers; and they can be potentially formed into casings, capsules, pouches, and bags. Related products include molded items of greater thickness. Coatings involve formation of films directly on the surface of the object they are intended to protect or enhance in some manner. In this sense, coatings become part of the product and remain on the product through use and consumption. Table 1.1 summarizes different uses for protein films and coatings, distinguishing between edible and biodegradable products.

EDIBLE VERSUS BIODEGRADABLE

Films and coatings based on proteins are edible and/or biodegradable, depending on formulation, formation method, and modification treatments. As long as food-grade proteins and other food-grade additives (e.g., plasticizers, acid or base, salts, and enzymes) are used and only protein changes due to heating, pH modification, salt addition, enzymatic modification, and water removal occur, the resulting film or coating is edible (Krochta and De Mulder-Johnston, 1997).

TABLE 1.1. Potential Uses of Proteins for Edible and/or Biodegradable Products.

Uses	Edible	Biodegradable
Food covers, wraps, and separation layers	X	X*
Food casings, pouches, bags, and labels	X	X*
Food coatings	X	
Food ingredient microcapsules	X	
Drug coatings, capsules, and microcapsules	X	
Disposable food service items (plates, cups, cutlery)		X
Trash bags (garden, restaurant)		X
Water-soluble bags for fertilizer, pesticides, etc.		X
Microcapsules for fertilizer, pesticides, etc.		X
Agricultural mulches		X
Paper coatings		X
Loose-fill packaging		X
Disposable medical products (gloves, gowns, etc.)		X
Disposable diapers		X

*Item must be removed before food consumption.

A small percentage of the population is allergic to one or more proteins, and the formation of films or coatings from proteins does not generally reduce allergenicity. Thus, proper labeling is essential so that the affected population can avoid the relevant protein. Beyond this issue, protein films and coatings can enhance the nutritional quality of foods, based on the protein content and the potential for incorporation of nutritional supplements. Because edible films and coatings can normally support microbial growth, proper attention must be paid to water activity, pH, temperature, atmosphere, and time. Addition of antimicrobials to edible films can protect the films and coatings, as well as the related foods, from microbial growth.

Edible films and coatings also are biodegradable. However, edibility is lost when the protein is reacted with other chemicals before or during film or coating formation (e.g., chemical grafting or chemical cross-linking), or when non-edible components are added to the film or coating. Biodegradable films and coatings for food packaging applications must be shown safe for such use (Krochta and De Mulder-Johnston, 1997). The challenge to biodegradable films and coatings for food packaging and other uses is that the film or coating must serve its function safely and effectively for the time needed. Only after the intended functional use has ended should biodegradation proceed. For the purposes of this chapter, biodegradable is taken to mean that the film or coating can be completely degraded by microorganisms in a composting process ultimately to only carbon dioxide, water, methane, and some biomass residue (Anonymous, 1993). A warm, moist environment with appropriate pH, nutrients, oxygen, and time for the appropriate microorganisms is necessary to allow the biodegradation process to proceed.

FUNCTIONS OF EDIBLE FILMS AND COATINGS

Most commonly, edible films and coatings are intended to function as a barrier to moisture, oxygen, flavor, aroma, and/or oil, thus improving food quality and shelf life. An edible film or coating may also provide some mechanical protection for a food, reducing bruising and breakage and thus improving food integrity. When an edible film or coating provides a moisture, flavor, aroma, or oil barrier between food components of different water activity, flavor, aroma, and/or oil content in a heterogeneous food, the quality and shelf life of the food are increased.

When an edible film or coating prevents exchange of moisture, oxygen, aroma, or oil between the food and the environment, the quality and shelf life of the food also are increased. However, when functioning in this manner, edible films and coatings are not normally intended to eliminate the need for non-edible protective packaging. Rather, they are intended to work with conventional packaging to improve product quality and shelf life. However, the amount of conventional protective packaging may be reduced (source reduction); and the remaining, simpler package may be more recyclable. In addition, after the package is opened, an edible film or coating can continue to protect the product.

The protective function of edible films and coatings may be enhanced with addition of antioxidants or antimicrobials to the film or coating. Depending on the nature of the food, an edible coating may also carry flavors, nutrients, etc., to enhance the quality of the food. Finally, an edible coating can provide additional important sensory attributes to foods, including gloss, color, and non-greasy, non-sticky, or non-color-bleeding surface. The various functions of edible films and coatings are summarized in Table 1.2.

RATIONALE FOR EDIBLE FILMS AND COATINGS

Every food suffers from at least one mass transfer problem, whether it is moisture migration, oxygen intrusion, aroma loss or gain, or oil migration. Given the range of barrier attributes that edible films and coatings can provide, foods can benefit with improved stability, texture, taste, and aroma. Incorpora-

TABLE 1.2. Possible Functions for Protein Films and Coatings.

Uses	Edible	Biodegradable
Barrier to moisture, oxygen, aroma, oil, etc.	X	X
Carrier of antimicrobial, antioxidant, etc.	X	X
Carrier of flavor, color, nutrients	X	
Resistance to mechanical forces	X	X
Product appearance enhancer (gloss, color, etc.)	X	

tion of antioxidants and/or antimicrobials that are control-released can further enhance food quality. Many foods also suffer from breakage and disintegration in manufacture, packaging, transportation, and use. The higher yield, easier handling, and improved appearance from integrity-enhancing coatings are additional potential advantages. Finally, consumers often associate food quality with appropriate gloss, color, and tactile feel, properties that edible coatings can affect. All of these features are of even greater importance because of increased consumer interest in quality, variety, and convenience. At the same time, food processors are interested in worldwide markets that demand longer shelf life and in providing products with a minimum of packaging, which is ultimately recyclable. Thus, these factors have combined to spark interest in exploring the film-formation, barrier, mechanical, and sensory properties of proteins and other materials.

FUNCTIONS OF BIODEGRADABLE FILMS AND COATINGS

As with edible films and coatings, biodegradable films and coatings can function as barriers to moisture, oxygen, flavor, aroma, and/or oil to protect the quality of food and other products from the environment. In contrast with edible films and coatings, the intent with a biodegradable film or coating is generally to totally replace the conventional synthetic packaging or other conventional synthetic product. A biodegradable film (e.g., pouch) or coating (e.g., on paper) may also need to provide some mechanical protection for a food, drug, or other product. If a biodegradable material is formed into related structures, such as food service items, the items must also have appropriate mechanical properties. The function of biodegradable films and coatings may also be enhanced with the addition of antioxidants or antimicrobials. Finally, the visual sensory attributes of biodegradable films and coatings, such as transparency, gloss, and color, are also important. The various potential functions of biodegradable protein films and coatings are summarized in Table 1.2.

RATIONALE FOR BIODEGRADABLE FILMS

Any successful replacement of conventional synthetic films and coatings with biodegradable alternatives reduces use of non-renewable resources and reduces waste through biological recycling (e.g., composting). Successful development of biodegradable films for packaging and other applications is most likely to occur when recovery of conventional synthetic polymer products for recycling or energy recovery is difficult. An example of where biodegradable alternatives, including food packaging, would be especially useful is for ships, which are now legally prohibited from dumping persistent waste at sea. Also, as municipalities increase availability of curbside pickup for large-scale municipal composting, interest in biodegradable packaging is increasing. Many mu-

nicipalities also encourage small-scale domestic composting, even providing necessary equipment. Biodegradable polymer films can also be run through domestic garbage disposals to the municipal waste treatment plant.

FILM AND COATING COMPOSITION

Materials available for forming films and film coatings fall generally into the categories of proteins, polysaccharides, lipids, and resins. A plasticizer must often be added to reduce film or coating brittleness. A surface-active agent is also often necessary to aid film or coating formation. Other constituents can include antioxidants and antimicrobials to enhance the film or coating effectiveness. The U.S. Code of Federal Regulations provides the status of protein, polysaccharide, lipid, resin, plasticizer, emulsifier, preservative, and antioxidant materials related to acceptable use (Baldwin, 1999).

PROTEINS

Proteins cover a broad range of polymeric compounds that provide structure or biological activity in plants or animals. Proteins are distinguished from polysaccharides because they are based on approximately 20 amino acid monomers, rather than just a few or even one monomer, such as glucose in the case of cellulose and starch. The amino acids are similar in containing an amino group ($-NH_2$) and a carboxyl group ($-COOH$) attached to a central carbon atom. However, each amino acid has a different side group attached to the central carbon that lends unique character to that amino acid. The side group can be non-polar (hydrophobic), polar uncharged (hydrophilic), positively charged at pH 7, or negatively charged at pH 7 (Cheftel et al., 1985).

Most proteins contain 100–500 amino acid residues. Depending on the sequential order of the amino acids (primary structure of the protein), the protein will assume different structures along the polymer chain (secondary structure of the protein), based on van der Waals, hydrogen bonding, electrostatic, hydrophobic, and disulfide cross-link interactions among the amino acid units (Cheftel et al., 1985). The tertiary protein structure reflects how the secondary structures organize relative to each other, based on the same types of interactions, to form overall globular, fibrous, or random protein structure. Finally, quaternary structure occurs when whole proteins interact with each other into associations to provide unique structure or biological activity.

The secondary, tertiary, and quaternary structures of proteins can be modified by various physical and chemical agents, including heat, mechanical treatment, pressure, irradiation, lipid interfaces, acids and alkalis, and metal ions (Cheftel et al., 1985). Such agents are often used in the formation of protein films and coatings to optimize protein configuration, protein interactions, and resulting film properties.

Protein film-forming materials derived from animal sources include collagen, gelatin, fish myofibrillar protein, keratin, egg white protein, casein, and whey protein. Protein film-forming materials derived from plant sources include corn zein, wheat gluten, soy protein, peanut protein, and cottonseed protein. Proteins that have successfully been formed into films and/or coatings are listed in Table 1.3 along with the solubility properties of the native proteins before formation into films or coatings.

POLYSACCHARIDES

Polysaccharide film-forming materials include starch and starch derivatives, cellulose derivatives, alginate, carrageenan, chitosan, pectinate, and various gums. Proteins can be combined with polysaccharides to modify film mechanical properties (Shih, 1994; Arvanitoyannis et al., 1996, 1997, 1998a, 1998b; Arvanitoyannis and Biliaderis, 1998).

LIPIDS

Edible lipids include beeswax, candelilla wax, carnauba wax, triglycerides (e.g., milkfat fractions), acetylated monoglycerides, fatty acids, fatty alcohols, and sucrose fatty acid esters. Edible resins include shellac and terpene resin. Because lipid and resin materials are not polymers, they do not generally form cohesive stand-alone films. However, along with often providing desirable gloss, they can be used to coat a food or drug surface to provide a moisture bar-

TABLE 1.3. Proteins Used for Edible and Biodegradable Films and Coatings.

Protein	Protein Solvents			
	Water	Acidic Water	Alkaline Water	Aqueous Ethanol
Collagen		X		
Gelatin	X			
Fish myofibrillar protein		X	X	
Keratin				X
Egg white protein			X	
Casein	X			
Whey protein	X			
Corn zein				X
Sorghum kafirin				X
Wheat gluten		X	X	X
Rice bran protein		X	X	
Soy protein	X		X	
Peanut protein			X	
Cottonseed protein			X	

rier or to provide the moisture-barrier component of a composite film. Composite films can consist of a lipid layer supported by a protein or polysaccharide layer, or lipid material dispersed in a protein or polysaccharide matrix (Krochta, 1997a).

PLASTICIZERS

Protein films and coatings are often quite stiff and brittle due to extensive interactions between protein chains through hydrogen bonding, electrostatic forces, hydrophobic bonding, and/or disulfide cross-linking. Relatively small molecular weight hydrophilic plasticizers are often added, which mainly compete for hydrogen bonding and electrostatic interactions with the protein chains. The result of plasticizer addition is a reduction in protein chain-to-chain interactions, a lowering of the protein glass transition temperature(s), and an improvement in film flexibility (lowering of film elastic modulus). Also, film elongation (stretchiness or ductility) increases, and film strength decreases. Unfortunately, plasticizers generally also decrease the film's ability to act as a barrier to moisture, oxygen, aroma, and oils. Plasticizers acceptable and generally used for protein edible films include glycerol, propylene glycol, sorbitol, sucrose, polyethylene glycol, fatty acids, and monoglycerides. Water is also an important plasticizer for protein films. Thus, film moisture content, as affected by the surrounding environment's relative humidity (RH), has a large effect on film properties. The presence of hydrophilic plasticizers such as glycerol attracts additional moisture and additionally impacts film properties. Plasticizers that are commonly used with protein films and coatings are summarized in Table 1.4.

EMULSIFIERS

Emulsifiers are surface-active compounds with both polar and non-polar character, which absorb at the water-lipid interface and reduce surface tension. To produce protein-lipid or polysaccharide-lipid composite films from aqueous solution, it is often necessary to add an emulsifier to allow dispersion of the lipid material in the solution. Also, for some food-coating applications, addition

TABLE 1.4. Plasticizers Commonly Used in Protein Films.

Glycerol
Propylene glycol
Triethylene glycol
Sorbitol
Sucrose
Polyethylene glycol

of a surface-active agent to a coating formulation may be necessary to achieve satisfactory surface wetting and spreading with the coating formulation and then adhesion of the dry coating. Some proteins are sufficiently surface-active that no emulsifier is necessary to form well-dispersed composite films or provide good surface wetting and adhesion.

OTHER FILM AND COATING ADDITIVES

As mentioned, edible films and coatings have the potential to be effective carriers and providers of antioxidants, antimicrobials, nutrients, flavors, and colors to enhance food safety, nutrition, and quality.

LABELING

When edible films and coatings become part of a processed food or pharmaceutical product in the U.S., their constituents must be clearly indicated on the product label as ingredients. This allows individuals to avoid products that contain ingredients about which they have concerns. When edible coatings used with fresh fruits and vegetables are sold without labeled packaging in the U.S., the coating composition must be clearly displayed in the vicinity of the coated produce. Regulations vary greatly among countries as to coating of fresh fruits and vegetables (Baldwin, 1999).

FILM AND COATING FORMATION

SOLVENT CASTING

Protein films and coatings are mainly formed by evaporation of solvent, usually water or aqueous ethanol, from a solution of the protein. With the exception of corn zein, wheat gluten, sorghum kafirin, and keratin, most film-forming proteins are soluble in water. Corn zein and wheat gluten films and coatings must be formed from aqueous ethanol solution or from an aqueous dispersion. Edible film and coating production that requires ethanol necessitates appropriate safety measures and attention to environmental release of solvent to the atmosphere. In this case, solvent recovery will become an increasingly important aspect of commercial operations. Table 1.3 lists the solvents required to solubilize various protein film-formers.

For formation of a film or coating, the protein is first dissolved in the solvent. If heating or pH adjustment enhances film formation and/or properties, this is done next. If a composite film or coating based on an emulsion is desired, a lipid material, and possibly a surfactant, is added. Next, the mixture is heated to above the lipid melting point and then homogenized. Degassing is an important

step to eliminate bubble formation in the final film or coating. Finally, the protein film or coating is formed by applying the prepared formulation to the desired casting or product surface and allowing the solvent to evaporate. Providing heated air at low humidity and high velocity increases drying rates.

For film production from such solvent casting, the formulation must be spread evenly on a surface that will release the film after drying. Formation of protein coatings on food products involves either dipping, spraying, enrobing, or panning the food with the coating formulation. These coating methods all require drying of solvent from a protein coating formulation after it is applied to the food surface.

Gelatin capsules cast from aqueous solutions are used widely in the pharmaceutical and nutritional supplement industries. Hard capsule halves are formed by dipping steel pins into gelatin solutions. After drying, the capsules are removed from the pins. A drug or supplement is then filled into a hard capsule half and interlocking halves are joined to form the full capsule. Soft gelatin capsules containing drugs or nutritional supplements are formed from two previously formed sheets of plasticized gelatin by injection of the drug or supplement at the moment when the two sheets are brought together between the rotating halves of roller dies.

EXTRUSION

Collagen casings and film-wraps for meat products are produced by extruding a viscous (4–10% solids) aqueous suspension of purified acidified collagen into a neutralizing coagulation bath, followed by washing, plasticizing, and drying. However, thermoplastic extrusion would be an attractive way to form protein casings and films, avoiding the need to add and then remove solvent by drying. Some research suggests that some proteins display thermoplastic behavior. However, inducing protein thermoplastic behavior generally has not been much explored or exploited for edible film production. Successful, efficient production of protein edible films using conventional extrusion equipment would certainly improve commercialization potential. However, little has been published on this approach.

PROPERTIES OF PROTEIN FILMS AND COATINGS

Table 1.5 lists the properties generally of interest with protein films and coatings, along with the pertinent testing method references.

BARRIER PROPERTIES

The main interest in edible films and coatings is generally based on their

TABLE 1.5. Properties of Protein Films and Coatings and Methods for Their Determination.

Film or Coating Property	Measurement Method
Film water vapor permeability	ASTM E 96 (ASTM, 1995d) ASTM F 1249 (ASTM, 1995e) (McHugh et al., 1993) (Gennadios et al., 1994b)
Film oxygen permeability	ASTM D 3985 (ASTM, 1995c) (Gilbert and Pegaz, 1969)
Film aroma permeability	(Hernandez et al., 1986) (Miller and Krochta, 1998a)
Film oil permeability	ASTM F 119 (ASTM, 1992) (De Mulder-Johnston, 1999)
Film tensile properties	ASTM 882 (ASTM, 1997)
Tensile strength	
Elastic (Young's) modulus	
Elongation	
Film/coating total solubility	(Handa et al., 1999)
Film/coating protein solubility	(Roy et al., 1999)
Film/coating gloss	ASTM D 523 (ASTM, 1995a)
Film/coating color	ASTM D 1925 (ASTM, 1995b)

potential to provide some combination of moisture, oxygen, flavor, aroma, color, or oil barrier for a food or drug, with a resulting increase in quality and shelf life. Thus, the permeability of edible films to these substances is of interest. Permeability is a steady-state property that describes the extent to which a permeating substance dissolves and then the rate at which the permeant diffuses through a film, with a driving force related to the difference in concentration of the permeant between the two sides of the films. Permeability is thus defined as

$$\text{Permeability} = \frac{\left(\text{steady-state rate of permeation through film in amount per time} \right) (\text{film thickness})}{(\text{film area}) \left(\text{permeant concentration or partial pressure difference across film} \right)}$$

where the concentration or partial pressure difference is between the phases adjacent to the two sides of the film.

The polar character of proteins determines the barrier properties of protein films. Protein films have high permeability to polar substances, such as water vapor, and low permeability to non-polar substances, such as oxygen, aromas and oils. Because plasticizers, including water, generally increase film permeability, permeability of protein films to both polar and non-polar substances increases with plasticizer content and RH.

The challenge in use of the barrier properties of protein films is to select the

protein, plasticizer, and film-formation conditions that optimize the desired barrier properties, while achieving other desirable properties such as film flexibility, strength, and solubility. Lack of knowledge and data on edible films, in general, still prevents design of edible films to desired specifications.

Tables 1.6 and 1.7 list selected protein film water vapor permeability (WVP) and oxygen permeability (OP) data, along with synthetic film data for comparison. It is important to note that plasticizer content (type and amount) and test conditions (temperature and RH) have important effects on film properties. Increasing plasticizer amount, temperature, and RH generally increases permeability. Thus, film properties should be compared at as near identical testing conditions as possible.

Water Vapor Permeability

Protein films have quite high WVP compared to edible waxes, which are often used as moisture barrier coatings on fruits, vegetables, confections, and drugs, and low-density polyethylene (LDPE) packaging film, which commonly is used to protect food and drugs from moisture (Table 1.6). Protein film WVP values are two to four orders of magnitude greater than that of LDPE. The aqueous ethanol-soluble proteins, corn zein and wheat gluten, and also fish myofibrillar protein appear to form films that have the lowest WVP among the proteins and are comparable to the WVP of cellulose derivatives. Table 1.6 also shows the effect of higher plasticizer concentration and higher RH test conditions on increasing WVP.

Oxygen Permeability

At low to intermediate RH, protein films have OP values that are lower than those of the polyethylenes (which are not good oxygen barriers), comparable to those of modest oxygen barriers such as polyesters, and approaching those of the best oxygen barriers, ethylene-vinyl alcohol copolymer (EVOH) and polyvinylidene chloride (PVDC) (Table 1.7). Protein films also appear to have somewhat lower OP than cellulose-based films. Table 1.7 also shows the effect of higher RH on increasing OP of protein films, which is similar to the effect of RH on the excellent synthetic oxygen-barrier EVOH. The low OP of protein films would appear to make them useful for coatings and pouches for oxygen-sensitive products.

Aroma and Oil Permeability

Limited research has been done on quantifying the aroma permeabilities of protein films. However, results showed that wheat gluten film was a better barrier to 1-octen-3-ol (mushroom aroma) than low-density polyethylene (LDPE)

TABLE 1.6. Water Vapor Permeability Values of Selected Protein Films Compared to Polysaccharide, Lipid, Wax, and Synthetic Polymer Films.

	Film*	Test Conditions**	Permeability g·mm/m ² ·d·kPa
Avena-Bustillos and Krochta (1993)	SC	25°C, 0/81% RH†	37
Banerjee and Chen (1995)	SC:Gly = 2:1	23°C, 55/72% RH†	310
Avena-Bustillos and Krochta (1993)	CC	25°C, 0/81% RH†	28
Banerjee and Chen (1995)	CC:Gly = 2:1	23°C, 55/77% RH†	190
Chick and Ustunol (1998)	RC:Gly = 1.4:1	38°C, 0/90% RH	45
Chick and Ustunol (1998)	LAC:Gly = 1.4:1	38°C, 0/90% RH	55
McHugh et al. (1994)	WPI:Gly = 4:1	25°C, 0/77% RH†	70
Banerjee and Chen (1995)	WPI:Gly = 2:1	23°C, 55/73% RH†	291
Anker et al. (1998)	WPI:Sor = 1:1	23°C, 50/72% RH†	211
Banerjee and Chen (1995)	WPC:Gly = 2:1	23°C, 55/74% RH†	255
Cuq et al. (1995)	FMP:Gly = 1.9:1	20°C, 100/0% RH	6.1
Gennadios et al. (1996a)	EMP:Gly = 3.3:1	25°C, 50/72% RH†	211
Stuchell and Krochta (1994)	SPI:Gly = 4:1	28°C, 0/78% RH†	39
Brandenburg et al. (1993)	SPI:Gly = 1.7:1	25°C, 50/100% RH	154
Jangchud and Chinman (1999)	PPC:Gly = 0.6:1	38°C, 0/50% RH	37
Park and Chinman (1995)	CZ:Gly = 4.9:1	21°C, 85/0% RH	9.6
Butler and Vergano (1994)	CZ:PEG+Gly = 5.9:1	25°C, 50/100% RH	47
Butler and Vergano (1994)	CZ:PEG+Gly = 2.6:1	25°C, 50/100% RH	107
Gontard et al. (1992)	WG:Gly = 5:1	30°C, 100/0% RH	5.1
Aydt et al. (1991)	WG:Gly = 2.4:1	26°C, 50/100% RH	108
Rankin et al. (1958)	Amylose	25°C, 100/0% RH	32
Hagenmaier and Shaw (1990)	HPMC	27°C, 0/85% RH	9.1
Kemper and Fennema (1984)	HPMC:PEG = 9:1	25°C, 85/0% RH	6.5
Hanlon (1992)	Methylcellulose	35°C, 90/0% RH	4.8

(continued)

TABLE 1.6 (continued).

	Film*	Test Conditions**	Permeability g·mm/m ² ·d·kPa
Lovegren and Feuge (1954)	Hydro, Peanut Oil	25°C, 100/0% RH	3.3
Lovegren and Feuge (1954)	AMG	25°C, 100/0% RH	1.9-13
Shellhammer and Krochta (1997a)	Tripalmitin	28°C, 0/100% RH	0.19
Shellhammer and Krochta (1997a)	Carnauba Wax	28°C, 0/100% RH	0.098
Shellhammer and Krochta (1997b)	Beeswax	26°C, 0/100% RH	0.089
Lovegren and Feuge (1954)	Paraffin Wax	25°C, 100/0% RH	0.019
Shellhammer and Krochta (1997b)	Candelilla Wax	25°C, 0/100% RH	0.012
Shellhammer and Krochta (1997a)	PVC	28°C, 0/100% RH	0.62
Shellhammer and Krochta (1997a)	PET	25°C, 0/100% RH	0.17
Shellhammer and Krochta (1997a)	LDPE	28°C, 0/100% RH	0.031

*SC = sodium caseinate; CC = calcium caseinate; RC = rennet casein; LAC = lactic acid casein; WPI = whey protein isolate; WPC = whey protein concentrate; FMP = fish myofibrillar protein; EWP = egg white protein; SPI = soy protein isolate; PPC = peanut protein concentrate; CZ = corn zein; WG = wheat gluten; HPMC = hydroxypropyl methylcellulose; Gly = glycerol; Sor = sorbitol; PEG = polyethylene glycol; AMG = acetylated monoglycerides; PVC = polyvinylchloride; PET = polyethylene terephthalate; LDPE = low-density polyethylene.

**RHs on top and bottom sides of film (top/bottom).

†Corrected RH shown for bottom of film.

TABLE 1.7. Oxygen Permeability Values of Selected Protein Films Compared to Polysaccharide and Synthetic Polymer Films.

	Film*	Test Conditions**	Permeability cm ³ ·μm/m ² ·d·kPa
Lieberman and Gilbert (1973)	Collagen	RT, 0% RH	<0.04-0.53†
Lieberman and Gilbert (1973)	Collagen	RT, 63% RH	29.3
Lieberman and Gilbert (1973)	Collagen	RT, 93% RH	890
McHugh and Krochta (1994a)	WPI:Gly = 2.3:1	23°C, 34% RH	20
McHugh and Krochta (1994a)	WPI:Gly = 2.3:1	23°C, 46% RH	55
McHugh and Krochta (1994a)	WPI:Gly = 2.3:1	23°C, 56% RH	132
Lim et al. (1998)	EWP:Gly = 1.9:1	25°C, 50% RH	70
Li et al. (1993)	SPI:Gly = 2.4:1	25°C, 0% RH	6.1
Gennadios et al. (1993a)	CZ:Gly = 5:1	25°C, 0% RH	12
Park and Chinnan (1995)	CZ:Gly = 4.9:1	30°C, 0% RH	31
Butler and Vergano (1994)	CZ:PEG+Gly = 2.6:1	25°C, 0% RH	65
Gennadios et al. (1993a)	WG:Gly = 2.5:1	25°C, 0% RH	6.1
Aydt et al. (1991)	WG:Gly = 2.5:1	38°C, 0% RH	6.7
Park and Chinnan (1995)	WG:Gly = 3.1:1	30°C, 0% RH	17
Anonymous (1990)	HPMC	24°C, 50% RH	272
Anonymous (1990)	Methylcellulose	24°C, 50% RH	97
Salame (1986)	LDPE	23°C, 50% RH	1870
Salame (1986)	HDPE	23°C, 50% RH	427
Hanlon (1992)	Polyester	23°C, 50% RH	16
Salame (1986)	VOH (70% VOH)	23°C, 0% RH	0.1
Salame (1986)	VOH (70% VOH)	23°C, 95% RH	12
Salame (1986)	PVDC-based films	23°C, 95% RH	0.4-5.1

*WPI = whey protein isolate; EWP = egg white protein; SPI = soy protein isolate; CZ = corn zein; WG = wheat gluten; HPMC = hydroxypropyl methylcellulose; Gly = glycerol; PEG = polyethylene glycol; AMG = acetylated monoglycerides; PVDC = polyvinylidene chloride; PET = polyethylene terephthalate; LDPE = low-density polyethylene.

**RT = room temperature.

†Based on values for PVDC-based films (Salame, 1986).

film or methylcellulose (MC) film (Debeaufort and Voilley, 1994). Other research results showed that whey protein film was better than vinylidene chloride copolymer (co-VDC) film and was comparable to ethylene-vinyl alcohol copolymer (EVOH) film as a barrier to limonene (citrus aroma) at similar conditions (Miller and Krochta, 1998b).

Similarly, limited data exist on oil permeability of protein films. Corn zein was shown to have excellent grease resistance, both as a film and as a coating on paper (Trezza and Vergano, 1994). These results showed the potential for fully compostable paper-based wraps and boxes for the food service industry. Research results also showed that whey protein film (De Mulder-Johnston, 1999) and whey protein coating on paper (Chan, 2000) provided excellent oil-barrier properties.

MECHANICAL PROPERTIES

The properties usually measured to mechanically characterize films are tensile strength (TS) (pulling force per film cross-sectional area required to break the film), elongation (E) (degree to which film can stretch before breaking), and elastic modulus (EM) (film stiffness as determined by ratio of pulling force/area to degree-of-film-stretch). Film toughness is approximated by the product of TS and E.

Protein films appear to have lower TS than most polysaccharide films and synthetic polymer films, and lower E than synthetic films (Table 1.8). Plasticizer level has a dramatic effect on film properties, with TS and EM decreasing and E increasing with increased plasticizer content. When plasticizer level is reduced to obtain protein film TS values similar to those of polyethylene (PE) or polypropylene (PP) films, the E values are one to two orders of magnitude lower than those of PE or PP. Thus, protein films have nowhere near the toughness of conventional synthetic polymer films. However, mechanical properties are generally sufficient to allow use of protein films for many products, such as casings, wraps, pouches, and coatings.

SOLUBILITY

Film and coating solubility is an important property that relates to intended use. In some cases, a film or coating readily soluble in water is desirable, such as a readily soluble pouch containing food ingredients. In other cases, a water-insoluble film or coating is preferred to provide some water resistance and improve food integrity. Film formers such as corn zein and wheat gluten that are not soluble in water produce films and coatings that are not water soluble. Protein film-formers that are soluble in water produce films of varying solubility, depending on the protein and the conditions of film formation and treatment. For example, native whey protein isolate produces totally water-soluble

TABLE 1.8. Tensile Properties of Selected Protein Films Compared to Polysaccharide and Synthetic Polymer Films.

Film*	Tensile Strength** MPa	Elongation** %	
Hood (1987)	Co:Ce:Gly = 3.4:0.8:1	3-11	25-50
Banerjee and Chen (1995)	SC:Gly = 2:1	3	30
Banerjee and Chen (1995)	CC:Gly = 2:1	4	1
Chick and Ustunol (1998)	RC:Gly = 1.4:1	5	224
Chick and Ustunol (1998)	LAC:Gly = 1.4:1	3	194
McHugh and Krochta (1994b)	WPI:Gly = 2.3:1	14	31
Banerjee and Chen (1995)	WPI:Gly = 2:1	6	23
Anker et al. (1999)	WPI:So: = 1.2:1	2-3	28-53
Banerjee and Chen (1995)	WPC:Gly = 2:1	3	21
Cuq et al. (1995)	FMP:Gly = 1.9:1	17	23
Gennadios et al. (1996a)	EWP:Gly = 3.3:1	4	12
Gennadios et al. (1996a)	EWP:Gly = 2:1	1	32
Lim et al. (1998)	EWP:Gly = 1.9:1	4	78
Gennadios et al. (1996a)	EWP:PEG = 1.7:1	3	88
Stuchell and Krochta (1994)	SPI:Gly = 4:1	13	17
Brandenburg et al. (1993)	SPI:Gly = 1.7:1	5	86
Jangchud and Chinnan (1999)	PPC:Gly = 0.6:1	1	74
Butler and Vergano (1994)	CZ:PEG + Gly = 3.6:1	7-16	43-198
Parris et al. (1998)	CZ:PEG = 2.33:1	6	44
Gennadios et al. (1993b)	WG:Gly = 2.7:1	2-4	170-208
Taylor (1986)	Cellophane	55-124	16-60
Anonymous (1990)	Methyl cellulose	62	10
Anonymous (1990)	HPMC	69	10
Wolff et al. (1951)	Amylose	70	23
Briston (1986)	LDPE	9-17	500
Briston (1986)	HDPE	17-35	300
Briston (1986)	PP	42	300
Briston (1986)	OPP	165	50-75
Briston (1986)	Polyester	175	70-100
Hanlon (1992); Houston (1986)	Polystyrene	35-55	1

*Co = collagen; Ce = cellulose; SC = sodium caseinate; CC = calcium caseinate; RC = rennet casein; LAC = lactic acid casein; WPI = whey protein isolate; WPC = whey protein concentrate; FMP = fish myofibrillar protein; EWP = egg white protein; SPI = soy protein isolate; PPC = peanut protein concentrate; CZ = corn zein; WG = wheat gluten; HPMC = hydroxypropyl methylcellulose; Gly = glycerol; PEG = polyethylene glycol; LDPE = low-density polyethylene; HDPE = high-density polyethylene; PP = polypropylene; OPP = oriented polypropylene.

**Test Conditions: -25°C, 50% RH.

films; but heat-denatured solutions of whey protein isolate produce films in which the protein is insoluble (Perez-Gago et al., 1999).

FILM-MODIFYING TREATMENTS

An important trend in recent years has been the investigation of many approaches for enhancing the barrier, mechanical, and solubility properties of protein films. Generally, these approaches involve modification of protein structure and/or interactions among protein molecules. Another approach has involved the creation of blended or composite films by introduction of polysaccharides or hydrophobic (lipid or wax) materials, respectively. Tables 1.9, 1.10, and 1.11 summarize the effects of selected treatments on protein film properties.

Plasticizer Type and Amount

As mentioned earlier, type and amount of plasticizer affects interactions between protein molecules, with resulting effect on film properties. Plasticizers are added to decrease film stiffness (EM) and increase film elongation (E). Normally, as the plasticizer amount increases, permeability values and E increase, while TS and EM decrease. At least with certain proteins, some plasticizers allow achievement of desired mechanical properties with less effect on barrier properties than alternatives (Table 1.9). This is an area worthy of additional research to allow more effective selection of plasticizers. Unfortunately, plasticizer selection is not capable of reducing protein film WVP by more than a factor of two to three. However, optimum selection of plasticizer can improve the already excellent oxygen barrier ability of protein films.

Protein Structure and Interaction

Depending on the method of protein recovery, protein fraction, film-solution treatment, and film-forming conditions, protein structure and interactions will be influenced. For example, different means of recovering casein can influence casein structure and thus film properties (Chick and Ustunol, 1998; Tomasula et al., 1998). On the other hand, the β -lactoglobulin fraction of whey protein gives the same film properties as the whole whey protein (Maté and Krochta, 1996a). Ultrasound treatment of film-forming solutions likely disrupts existing protein interactions, thus resulting in increased molecular interaction (Banerjee et al., 1996). Modified protein interaction can also occur due to film-forming solution pH adjustment (Gontard et al., 1992; Brandenburg et al., 1993) or film adjustment to the protein isoelectric point (pI) (Avena-Bustillos and Krochta, 1993; Gennadios et al., 1993c). Heat treatment of film-forming solution causes denaturation due to intramolecular disulfide

TABLE 1.9. Effect of Plasticizer Type and Amount on Properties of Selected Protein Films.

Reference	Film*	Treatment	WVP** g·mm/ m ² ·d·kPa	OFT cm ³ ·µm/ m ² ·d·kPa	TS†, MPa	EM‡, MPa	Et, %
McHugh and Krochta (1994b)	WPI:Gly = 2.3:1	Gly plasticizer		76	14	490	31
McHugh and Krochta (1994b)	WPI:Gly = 5.7:1	Gly plasticizer		19	29	1100	4
McHugh and Krochta (1994b)	WPI: Sor = 2.3:1	Sor plasticizer		4.3	14	1040	2
Gennadios et al. (1996a)	EWP:Gly = 3.3:1	Gly plasticizer	211		4		12
Gennadios et al. (1996a)	EWP:Gly = 2:1	Gly plasticizer	256		1		32
Gennadios et al. (1996a)	EWP:PEG = 2:1	PEG plasticizer	149		4		60
Gennadios et al. (1996a)	EWP: Sor = 2:1	Sor plasticizer	118		4		15
Siew et al. (1999)	SC:Gly§	Gly plasticizer	4.3		5		81
Siew et al. (1999)	SC:PEG§	PEG plasticizer	8.6		12		41

*WPI = whey protein isolate; EWP = egg white protein; SC = sodium caseinate; Gly = glycerol; Sor = sorbitol; PEG = polyethylene glycol.

**WVP = water vapor permeability. Test condition: 25°C, 50%RH-60% RH (film top/bottom).

†OP = oxygen permeability. Test condition: 23°C, 50% RH.

‡TS = tensile strength; EM = elastic modulus; E = elongation. Test condition: ~23°C, 50% RH.

§§Same moles plasticizer:oxygen atoms/moles SC.

TABLE 1.10. Effect of Protein Structure and Interactions on Properties of Protein Films.

Reference	Film*	Treatment	WVP** g-mm/ m ² -d-kPa	Op** cm ³ - μ m/ m ² -d-kPa	TS† MPa	EM† MPa	Et %	Solubility %
Avena-Bustillos and Krochta (1993)	SC		37					100†
Avena-Bustillos and Krochta (1993)	SC	CaCl ₂ -treated film	21					100†
Avena-Bustillos and Krochta (1993)	SC	pH 4.6 (pI)-treated film	21					0
Banerjee et al. (1996)	SC:Gly = 2:1		13		3		30	
Banerjee et al. (1996)	SC:Gly = 2:1	Ultrasounded film solution	14		15		23	
Tomasula et al. (1998)	CC:Gly = 2.3:1		76		2	11	67	100
Chick and Ustunol (1998)	CO ₂ -C:Gly = 2.3:1		53		1	10	50	17
Chick and Ustunol (1998)	RC:Gly = 1.4:1	CO ₂ -precipitated casein	45	1.8§	5		224	
Chick and Ustunol (1998)	RC:Sor = 1.4:1	Rennet-precipitated casein	40	1.0§	15		18	
Chick and Ustunol (1998)	LAC:Gly = 1.4:1	Rennet-precipitated casein	55	0.7§	3		194	
Chick and Ustunol (1998)	LAC:Sor = 1.4:1	Lactic acid-precipitated casein	34	0.8§	12		51	
Maté and Krochta (1996a)	WPI:Gly = 2.3:1	Lactic acid-precipitated casein	92	27§§				
Maté and Krochta (1996a)	β -Lg:Gly = 2.3:1	β -Lg separated from WPI	94	30§§				
Alcantara et al. (1998)	WPI:Gly = 1.5:1	21°C, 50% RH film drying	51		1	43	38	
Alcantara et al. (1998)	WPI:Gly = 1.5:1	95°C, 30% RH film drying	38		3	136	27	
Miller et al. (1997)	WPI:Gly = 4:1		89		11	372	33	
Miller et al. (1997)	WPI:Gly = 4:1		40		46	1200	3	
Pérez-Gago et al. (1999)	WPI:Gly = 2.3:1	80°C, 60% RH-cured film	121		3	100	7	100
Pérez-Gago et al. (1999)	WPI:Gly = 2.3:1	Room-temp. film solution	119		7	199	41	25
Pérez-Gago et al. (1999)	WPI:Gly = 2.3:1	90°C-treated film solution						

TABLE 1.10 (continued).

Reference	Film*	Treatment	WVP** g-mm/ m ² -d-kPa	Op** cm ³ - μ m/ m ² -d-kPa	TS† MPa	EM† MPa	Et %	Solubility %
Gennadios et al. (1996a)	EWP:Gly = 2.1:1	Enzyme-treated film solution	256		1		32	
Lim et al. (1998)	EWP:Gly = 1.9:1	pH 2 film solution			4		78	50
Gontard et al. (1992)	WG:Gly = 5:1	pH 6 film solution	8.4	70§				100
Gontard et al. (1992)	WG:Gly = 5:1		6.5					
Gennadios et al. (1993c)	WG:Gly = 2.5:1	CaCl ₂ -treated film	4.8	3.9§	3		238	
Gennadios et al. (1993c)	WG:Gly = 2.5:1		4.2	3.7§	4		162	
Gennadios et al. (1993c)	WG:Gly = 2.5:1	pH 7.5 (pI)-treated film	4.2	4.5§	3		215	
Ali et al. (1997)	WG:Gly = 3:1		167		4		188	
Ali et al. (1997)	WG:Gly = 3:1	95°C-cured film	105		16		10	
Parris et al. (1998)	CZ		15		11	551	3	
Parris et al. (1998)	CZ		13		17	1213	2	
Brandenburg et al. (1993)	SPI:Gly = 1.7:1	Dialdehyde-starch added		4.5§	3		67	
Brandenburg et al. (1993)	SPI:Gly = 1.7:1	pH 6 film solution	262	1.6§	5		86	
Stuchell and Krochta (1994)	SPI:Gly = 4:1	pH 12 film solution	154					30
Stuchell and Krochta (1994)	SPI:Gly = 4:1	Room-temp. film solution	44		11	928	10	27
Stuchell and Krochta (1994)	SPI:Gly = 4:1	85°C-treated film solution	39		13	992	17	37
Stuchell and Krochta (1994)	SPI:Gly = 4:1	Enzyme-treated film solution	31		8	1503	1	17
Gennadios et al. (1996b)	SPI:Gly = 1.7:1		311		3		112	
Gennadios et al. (1996b)	SPI:Gly = 1.7:1	95°C-cured film	141		14		23	1
Gennadios et al. (1998b)	SPI:Gly = 2:1		173		4		124	
Gennadios et al. (1998b)	SPI:Gly = 2:1	UV-radiation-treated film	216		6		86	

(continued)

TABLE 1.10 (continued).

Reference	Film*	Treatment	WVP** g/mm/ m ² ·d·kPa	OP** cm ³ ·µm/ m ² ·d·kPa	TST MPa	EMT MPa	Et %	Solubility %
Were et al. (1999)	SPI:Gly = 3:1	Cysteine in film solution PGA in film solution 70°C film drying 90°C film drying Gossypol, etc. in film solution	216	0.68\$	4			
Were et al. (1999)	SPI:Gly = 3:1		130	0.58\$	7			
Rhim et al. (1999)	SPI:Gly = 2:1		216		3		172	28
Rhim et al. (1999)	SPI:Gly = 2:1		173		5		135	26
Jangchud and Chinnan (1999)	PPC:Gly = 0.6:1		37	15\$	1		74	
Jangchud and Chinnan (1999)	PPC:Gly = 0.6:1		10	2.1\$	4		146	
Marquie et al. (1995)	CSF:Gly = 4:1							100
Marquie et al. (1995)	CSF:Gly = 4:1							100
Marquie et al. (1995)	CSF:Gly = 4:1							100

*SC = sodium caseinate; CC = calcium caseinate; RC = rennet casein; LAC = lactic acid casein; WPI = whey protein isolate; β -Lg = β -Lactoglobulin; EWP = egg white protein; WG = wheat gluten; CZ = corn zein; SPI = soy protein isolate; PPC = peanut protein concentrate; CSF = cottonseed flour; PGA = propylene glycol alginate; Gly = glycerol; Sor = sorbitol.

**WVP = water vapor permeability; OP = oxygen permeability. Test conditions different among references.

†TS = tensile strength; EM = elastic modulus; E = elongation. Test condition: -23°C, 50% RH.

‡Krochta et al. (1988).

\$0% RH.

§850-55% RH.

TABLE 1.11. Effect of Blended and Composite Film Structures on Properties of Protein Films.

Reference	Film*	Treatment	WVP** g/mm/ m ² ·d·kPa	OP** cm ³ ·µm/ m ² ·d·kPa	TST MPa	EMT MPa	Et %	Solubility %
Arvanitoyannis et al. (1996)	Starch:SC = 1:1:1	Starch:SC blend film	4.7	432	13	30	28	
Arvanitoyannis et al. (1996)	Starch:SC = 7.5:1	Starch:SC blend film	6.0	2160	31	26	9	
Avena-Bustillos and Krochta (1993)	SC		37					100†
Avena-Bustillos and Krochta (1993)	CC:BW = 1:7:1	CC:BW emulsion film	3.6					100†
McHugh and Krochta (1994c)	WPI:BW = 3:5:1	WPI:BW emulsion film	52					
McHugh and Krochta (1994c)	WPI:BW:Gly = 3:5:1.8:1	WPI:BW emulsion film	5.3					
Shellhammer and Krochta (1997c)	WPI:Gly = 15:1	WPI:BW emulsion film	46		28	1670	2	
Shellhammer and Krochta (1997c)	WPI:Gly = 3:1	WPI:BW emulsion film	4.8		11	950	2	
Shellhammer and Krochta (1998)	WPI:Gly = 6:3:1	WPI:BW emulsion film	24		4		5	
Shellhammer and Krochta (1998)	WPI:Gly = 6:3:1	WPI:BW emulsion film	6.0		4		5	
Gennadios et al. (1993c)	WG:Gly = 2.5:1	Annealed WPI:BW film	4.8	3.9	2.6		238	
Gennadios et al. (1993c)	WG:MO:Gly = 2.5:0.6:1	WG:MO emulsion film	3.5	3.3	2.2		267	
Gontard et al. (1994)	WG:Gly = 5:1	WG:BW emulsion film	8.3					
Gontard et al. (1994)	WG:BW:Gly = 5:2:1	WG:BW emulsion film	3.0					
Gontard et al. (1995)	BW/WG:DTM:Gly = 7/5:2:1	BW/WG:DTM bilayer film	0.036					
Gennadios et al. (1998a)	SPI:Gly = 1:1	SPI:OA emulsion film	151		4.4	70	141	26
Gennadios et al. (1998a)	SPI:Gly:OA = 1:2:1.2:1	SPI:OA emulsion film	49		1.6			13
Park et al. (1994c)	CZ:G+P = 2:1	CZ:PA composite film	20					
Park et al. (1994c)	CZ:G+P/MC:Gly = 2:1/9:1	CZ/MC bilayer film	60		33		28	
Park et al. (1994c)	CZ:PA:G+P/MC:Gly = 2:1:1/9:1	CZ:PA/MC bilayer film	1.6		18		65	

*SC = sodium caseinate; CC = calcium caseinate; WPI = whey protein isolate; WG = wheat gluten; CZ = corn zein; MC = methylcellulose; Gly = glycerol; Sor = sorbitol; PEG = polyethylene glycol; G+P = Gly+PEG; BW = beeswax; MO = mineral oil; DTM = diacetyl tartaric ester of monoglycerides; OA = oleic acid; PA = palmitic acid.

**WVP = water vapor permeability; OP = oxygen permeability. Test conditions different among papers.

†TS = tensile strength; EM = elastic modulus; E = elongation. Test condition: -23°C, 50% RH.

‡Krochta et al. (1988).

bond breakage. The result is opportunity for protein cross-linking due to intermolecular disulfide bond formation and changed film properties. In fact, most protein film formation involves such heat treatment of film-forming solutions. The effect on some protein film properties is dramatic (Perez-Gago et al., 1999). Protein cross-linking can also occur due to an enzyme (Stuchell and Krochta, 1994; Lim et al., 1998), addition of a cross-linking agent (Avena-Bustillos and Krochta, 1993; Gennadios et al., 1993a; Marquie et al., 1995; Parris et al., 1998; Rhim et al., 1999; Were et al., 1999), or ultraviolet radiation (Gennadios et al., 1998b). Film drying or curing conditions can also modify protein structure and interactions (Gennadios et al., 1996b; Ali et al., 1997; Miller et al., 1997; Alcantara et al., 1998; Jangchud and Chinnan, 1999).

Modifying protein structure and interaction by the methods discussed above can reduce protein film WVP by a factor of two to four (Table 1.10). Such change is impressive, but not sufficient to convert protein films to good moisture barriers. However, reduction of protein film OP by enhancing protein structure and interaction improves the already excellent oxygen barrier properties of protein films (Table 1.10).

The largest effect of changes in protein structure and interaction can be on film mechanical properties and film solubility. Protein film mechanical properties can change by several factors, and the film protein content can go from totally soluble to totally insoluble (Table 1.10).

Blended and Composite Film Structures

A polysaccharide material, such as starch, can be combined with protein to produce a blended film system. Limited data exist on such blended films (Arvanitoyannis et al., 1996, 1997, 1998a, b; Arvanitoyannis and Biliaderis, 1998). It appears there is little effect on film WVP, but that addition of polysaccharide may increase film OP and TS and decrease film E (Table 1.11).

The greatest reduction in protein film WVP is achieved by addition of a lipid or wax to the film structure. The protein provides structural integrity for the film while the hydrophobic lipid or wax provides the moisture barrier. Dispersing a lipid or wax in the protein film structure to achieve an "emulsion film" can reduce the film WVP by an order of magnitude. However, this still places the film's WVP one to three orders of magnitude greater than the WVP of the pure lipid or wax, or of a PE film. Thus far, the only way to achieve a good moisture barrier is to laminate a preformed protein or polysaccharide film with a layer of lipid or wax to achieve a bilayer film (Table 1.11). While addition of a lipid or wax to a protein film can reduce film WVP, such addition usually increases film OP, reduces film TS and EM, and increases film E (Table 1.11). Also, the possibility of resulting cracks and pinholes in the film increases.

PROTEIN FILM AND COATING APPLICATION OPPORTUNITIES

PROTEIN FILM AND COATING APPLICATION GOALS

The goal of biodegradable films and other biodegradable products is simple: replace existing synthetic, non-biodegradable products for uses such as those listed in Table 1.1 at the lowest cost possible. However, edible films and coatings are normally not meant to be replacements for existing non-edible films and coatings. The main focus is on improving food quality and shelf life by reducing the effect of moisture, oxygen, migration, etc., protecting food from microbes, maintaining food product integrity, and enhancing product appearance. However, this must be related to the cost of coating materials and to the cost of the coating process. Evaluating the financial benefit of improved food quality and shelf life is difficult, but must be done. In addition, potential savings related to reduction of packaging may factor into the analysis. Finally, if the resulting packaging is simpler and, thus, more recyclable, this advantage should also be included in the analysis. Edible film and coating application goals are listed in Table 1.12.

EDIBLE FILM AND COATING COMMERCIAL APPLICATIONS

Table 1.13 lists commercial edible film and coating materials along with intended applications. These include forming an edible film as a coating directly on a food or drug product, as well as filling a food or drug product into a preformed edible film casing, pouch, or capsule. Table 1.14 lists the functions edible coatings serve in different food products.

Edible wax and shellac coatings are used on fruits and vegetables to prevent moisture loss and improve appearance. Wax, shellac, and zein coatings are used on confections to provide moisture resistance and improve appearance. Sucrose esters of fatty acids are used in formulations to reduce respiration, moisture loss, and skin marking and bruising in fruits and vegetables.

Hydroxypropyl methylcellulose (HPMC), hydroxypropyl cellulose (HPC), methylcellulose (MC), shellac, and zein coatings and gelatin capsules are used for pharmaceuticals to improve product appearance, structural integrity, and ingestibility, as well as to protect against moisture and oxygen. HPMC and MC

TABLE 1.12. Edible Film and Coating Application Goals.

<p>Reduce oxygen, aroma, oil, and/or moisture migration. Maintain food product integrity. Enhance food product appearance. Minimize cost of coating materials and coating process. Reduce packaging needs.</p>
--

TABLE 1.13. Edible Film and Coating Commercial Applications.*

Waxes and oils	Coatings for fresh produce, dried fruit, confections, supplements, and drug tablets
Shellac	Coatings for fresh produce, confections, supplements, and drug tablets
Sucrose and dextrose	Coatings for confections, supplements, and drug tablets
Fatty acid sucrose esters	Coatings for fresh produce
HPMC, HPC, MC	Coatings for supplements and drug tablets
HPMC, MC	Coatings for fried foods
MC	Coatings for fresh produce
HPMC	Pouches for dry food ingredients
Starch	Coatings for drug tablets
Starch, dextrin, and gums	Coatings for confections and fried foods Seasoning adhesives for nuts, snacks, and cereals Flavor encapsulation
Corn zein	Coatings for confections, supplements, and drug tablets
Collagen	Wraps and casings for meat products
Gelatin	Capsules for supplements and drugs Flavor encapsulation

*Adapted from Trezza (1999).

are also used for coatings on fried foods to reduce moisture loss and fat gain. MC is also used in commercial formulations to extend the life of fresh whole or cut fruits and vegetables. HPMC pouches are marketed for delivery of pre-measured food ingredients to food formulations with subsequent dissolution of the pouch.

Starch-based materials are marketed for coating drug tablets. Starch and dextrin formulations are also marketed as protective coatings, integrity maintainers, appearance enhancers, and seasoning adhesives for nuts, snacks, cereals, and meats.

Collagen casings and wraps inhibit moisture loss and oxygen transport and provide structural integrity for meat products.

EDIBLE FILM AND COATING POTENTIAL APPLICATIONS

While the potential applications in Tables 1.13 and 1.14 are noteworthy, actual applications represent a small fraction of the foods that could benefit from an edible film or coating. Every food suffers from at least one mass transfer problem, whether it be moisture migration, oxygen intrusion, aroma loss, or oil migration. Many foods could also benefit from improvement in integrity or appearance. However, applications have not become more widespread because commercial film and coating materials are either too expensive or too difficult to form, and/or commercial materials do not function efficiently. Thus, extensive research continues in this area. Certain new edible film and coating materials, including proteins, are targeted for replacing materials currently used in ex-

TABLE 1.14. Functions Provided by Edible Coatings for Foods, Supplements, and Drugs.*

	Confections and Gum	Fresh Produce	Snack Foods	Fried Foods	Encapsulated Flavors	Nutritional Supplements	Drug Tablets
Gloss	X	X		X		X	X
Mechanical integrity, texture enhancer	X		X	X		X	X
Ingredient carrier, seasoning adhesive		X	X	X	X	X	X
Moisture barrier	X	X	X	X	X	X	X
Oxygen barrier			X	X	X	X	X
Oil barrier			X	X	X	X	X
Aroma barrier	X		X	X	X	X	X
Color carrier	X		X			X	X
Modified release	X						

*Adapted from Trezza (1999).

TABLE 1.15. Investigated Applications and Functions of Edible Protein Films and Coatings.

Protein	Reference	Application	Function
Collagen	Farouk et al. (1990)	Beef round steak	Exudate barrier and oxygen barrier overwrap
	Conca and Yang (1993); Conca (1994); Rice (1994)	Beef cubes	Moisture and oxygen barrier wrap
Gelatin	Klose et al. (1952)	Cut-up turkey meat	Oxygen barrier and antioxidant carrier
	Keil et al. (1960); Keil (1961) Shifrin (1968)	Meat products	Mold prevention, oxygen barrier, handling protection
Corn Zein (CZ)	Whitman and Rosenthal (1971)	Yogurt	Fruit separation
	Moorjani et al. (1978)	Meat cuts	Oxygen and moisture barrier
	Olson and Zoss (1985)	Smoked chicken meat	Moisture barrier
	Guilbert (1988)	Battered and breaded meats	Frying oil barrier
	Mickus (1955)	Model food	Antimicrobial carrier
	Georgevits (1967)	Rice	Vitamin adhesion
	Turbak (1972)	Dried foods	Water-soluble pouch
	Meyer and Spencer (1973)	Sausage	Moisture and oxygen barrier casing
	Wu and Schwartzberg (1992)	Eggs	Moisture and bacteria barrier, shell strength increase
	Trezza and Vergano (1994)	Popcorn	Moisture barrier
	Park et al. (1994a, b)	Paper	Grease barrier
	Park et al. (1996)	Tomatoes	Moisture and oxygen-carbon dioxide barrier
Herald et al. (1996)	Apples and pears	Oxygen-carbon dioxide barrier	
Wong et al. (1996)	Cooked turkey	Oxygen barrier and antioxidant carrier wrap	
Mallikarjunan et al. (1997)	Shell eggs	Moisture and gas barrier, shell strength increase	
		Starchy foods	Moisture and oil barrier

TABLE 1.15 (continued).

Protein	Reference	Application	Function
CZ-Acetylated Monoglyceride	Cosler (1957, 1959); Alikonis (1979)	Confections	Oxygen, lipid, moisture barrier; antioxidant carrier; stickiness prevention
	Cosler (1958a, b, c); Alikonis and Cosler (1961)	Almonds, peanuts, pecans, walnuts	Oxygen, lipid, moisture barrier; antioxidant carrier
	Torres and Karel (1985); Torres et al. (1985)	Intermediate-moisture food	Preservative carrier
CZ-Vegetable Oils	Andres (1984)	Nuts, confections, pharmaceuticals	Oxygen and moisture barrier; antioxidant carrier
	Gunnerson and Bruno (1990)	Dried fruit	Antioxidant carrier and stickiness prevention
CZ-Vegetable Wax-Oil Laminates	Noznick and Buncius (1967)	Nuts	Salt binding
	Mullen (1971); Turbak (1972); Schilling and Burchill (1972)	Sausage	Moisture and oxygen barrier casing
	Georgevits (1967)	Dried foods	Water-soluble pouch
Soy Protein	Turbak (1972)	Sausage	Moisture and oxygen barrier casing
	Wong et al. (1996)	Shell eggs	Moisture and gas barrier; shell strength increase
Casein	Georgevits (1967)	Dried foods	Water-soluble pouch
	Hirasa (1991)	Frozen fish	Moisture barrier
Casein-Acetylated Monoglyceride	Avena-Bustillos et al. (1994a)	Zucchini	Moisture barrier
	Avena-Bustillos et al. (1997)	Celery sticks	Moisture barrier
Casein-Stearic Acid	Avena-Bustillos et al. (1993, 1994b)	Peeled carrots	Moisture retention

(continued)

TABLE 1.15 (continued).

Protein	Reference	Application	Function
Whey Protein (WP)	Rosenberg and Young (1993); Moreau and Rosenberg (1993)	Fat microencapsulation	Oxygen barrier
	Stuchell and Krochta (1995)	Frozen salmon	Antioxidant carrier
	Maté and Krochta (1996b, 1998); Maté et al. (1996)	Peanuts	Oxygen barrier
WP, WP-Acetylated Monoglyceride	Alcantara (1996)	Freeze-dried chicken	Handling protection
Albumen	Chen (1995)	Breakfast cereal, raisins, diced cheese, peas	Moisture barrier and stickiness prevention
	Wong et al. (1996)	Shell eggs	Moisture and gas barrier; shell strength increase
Albumen and Gelatin	Suderman et al. (1981)	Chicken parts	Breading adhesion
Albumen and Soy Protein	Watters and Brekke (1961); Bolin (1976)	Raisins	Moisture barrier
Albumen, Soy Protein, and Wheat Gluten	Baker et al. (1972)	Battered meats, etc.	Batter adhesion
Casein, Gelatin, and Soy Protein or CZ/Fatty Acid	Cole (1969)	Dried fruits and vegetables	Moisture and oxygen barrier
Amylose Ester			
Albumen, Casein, Gelatin, and Corn Zein	Johnson (1969)	Nuts	Color carrier
Albumen, Casein, Gelatin, and Soy Protein- Vegetable Oil	Durst (1967)	Baked and fried goods, chocolate	Oxygen and moisture barrier

isting applications. Beyond existing applications, edible films and coatings are generally seen as having considerable potential for applications far beyond current usage for improving product quality and, in some instances, reducing use of synthetic packaging films. Several reviews list edible protein film and coating applications that have been explored over the years (Baker et al., 1994; Baldwin, 1994; Gennadios et al., 1994a, 1997; Krochta, 1997c; Krochta and De Mulder-Johnston, 1997).

Table 1.15 lists protein film and coating research that has been conducted to provide improved materials and coating formation for existing applications, as well as to explore new food applications. Compared to the large number of studies performed on film formation and properties (see Tables 1.6–1.11), a relatively small number of application studies have been performed. Thus, information is generally lacking on approaches to coating foods, as well as the resulting effectiveness of edible films and coatings in food systems. This makes it very difficult for food processors to decide on the “value-added” merit of an edible film or coating relative to the additional cost involved.

SUMMARY AND CONCLUSIONS

Based on their chemical composition and structure, proteins make excellent oxygen, aroma, and oil barrier films and coatings at low to intermediate RH, similar to the best synthetic barrier films. Research on the effect of plasticizer type and amount may provide opportunities for achieving desired mechanical properties while further improving these barrier properties.

The hydrophilic nature of proteins results in high film and coating WVP, which is several orders of magnitude greater than synthetic moisture barrier films. Increasing protein interaction (e.g., chain cross-linking) can reduce the WVP by several factors, but nowhere near that required to achieve a good moisture barrier. The main effects of such protein modifications are usually to increase film strength and stiffness, and decrease film elongation and solubility. However, addition of lipid or wax materials improves the moisture barrier ability. Additional research on protein-lipid/wax composite film formation and properties is needed to improve the performance and reduce the cost of protein-based films and coatings as moisture barriers.

Protein films have mechanical properties that, overall, are inferior to those of synthetic and polysaccharide films but are sufficient for most applications. Addition of polysaccharide material to protein film can improve film strength, elongation, and toughness. Additional research in this area will likely help optimize properties of protein-polysaccharide films and coatings.

Much good research has been devoted to forming various protein films and quantifying the protein film properties. However, it is a large step from that point to determination of the film's effectiveness in improving the quality of foods or other products. Considerable research is needed to improve the effi-

ciencies of forming protein films as coatings on foods and to quantify the effects of the coatings on food quality using both instrumental and sensory evaluation. Investigation of protein coating adhesion, gloss, and color as affected by coating formulation and coating process is needed. Demonstration of protein coating effectiveness at reducing moisture change, oxidation, aroma, and oil migration, and improving food integrity is necessary to help protein coatings reach their full potential. Recent research on coating fruits and vegetables, meats, eggs, starch foods, nuts, other dry foods, and paper has provided needed data and helped demonstrate the potential of protein coatings. Research on the effectiveness of adding antioxidants, antimicrobials, and other additives to protein films and coatings is also needed.

Advantages would result for certain food applications from the ability to extrude protein films as an alternative to solvent casting. Achieving such capability will require research ranging from establishing the thermal properties of proteins to extrusion conditions suitable for optimum film formation and properties. Such capability is also essential for realizing the potential of protein films and related structures for biodegradable products.

Continuing interest in increasing food quality, reducing use of limited resources, and reducing the environmental impact of synthetic polymers will likely result in increased use of edible and biodegradable films and coatings in the future. To achieve this potential, continuing advances in formation, properties, and economics of edible and biodegradable protein films and coatings are necessary.

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