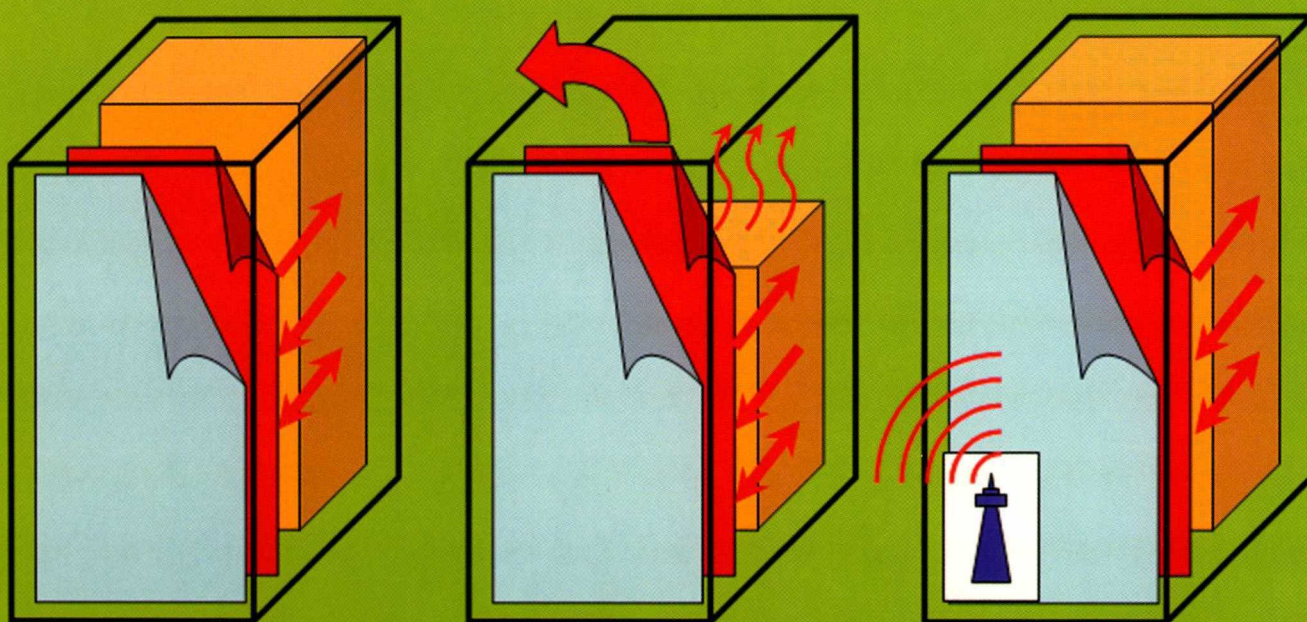


Innovations in Food Packaging



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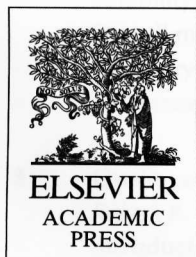


Innovations in Food Packaging

Edited by

Jung H. Han

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Edible films and coatings from plant origin proteins

Roberto A. Buffo and Jung H. Han

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Introduction

The 1990s saw a remarkable increase in research efforts for the development of biopolymer films and coatings from protein, polysaccharide, and lipid materials. The qualities of renewability, degradability, and edibility make such films particularly appealing for food and non-food packaging applications. Moreover, wide commercialization of biopolymer films would provide a value-added innovative use for traditional agricultural commodities as sources of film-forming materials. This chapter discusses the film formation ability and associated functional properties of a number of plant proteins, namely those extractable from corn, soybean, wheat, cottonseed, and other crops.

Zein films and coatings

Zein comprises a group of prolamins found in corn endosperm. It accounts for 50% or more of total endosperm protein, occurring in small and compact bodies embedded in the glutelin protein matrix and distributed mainly in the outer layers of the endosperm (Dombrink-Kurtzman and Bietz, 1993).

Commercial zein is a by-product of the corn wet-milling industry. After cleaning, corn is steeped in water containing sulfur dioxide to soften the grains. Coarse milling separates the hulls and germ from the endosperm, which is further milled into a fine slurry. Centrifugal separation of starch from the endosperm slurry leaves a protein-rich mass, or corn gluten meal, from which zein is extracted with aqueous alcohol and dried to a granular powder (Padua and Wang, 2002).

Zein occurs as aggregates linked by disulfide bonds in whole corn. Those bonds may be cleaved by reducing agents during extraction or wet-milling operations (Reiners *et al.*, 1973). Based on solubility differences, zein consists of three protein fractions, α -zein, β -zein and γ -zein, α -zein being predominant (75–85% of total zein) (Esen, 1987).

Coatings

Zein is one of a few proteins, such as collagen and gelatin, used commercially as an edible coating. Zein coatings are used as oxygen, lipid, and moisture barriers for nuts, candies, confectionery, and other foods (Andres, 1984), and for controlled ingredient release and protection in pharmaceutical tablets (Gennadios and Weller, 1990).

Zein coatings are prepared in three steps. Zein powder is dissolved in warm, aqueous ethyl alcohol or isopropanol. Approved plasticizers such as propylene glycol or glycerin are added to increase coating flexibility. The products to be coated are dipped into, sprayed with or brushed with the zein–plasticizer solution. Antioxidants such as BHT or BHA are added to prevent lipid oxidation, and vegetable oils to enhance film shine. The coating is formed on the product surface upon solvent evaporation (Andres, 1984; Gennadios and Weller, 1990; Park *et al.*, 1994a, 1994b; Wong *et al.*, 1996).

Thickness is a critical property of coatings that becomes a quality-control bottleneck in manufacturing, as it decisively influences physical and barrier properties. To measure thickness, a direct observation of a thin section of the coated product under a light microscope is preferred over an indirect estimation (Park *et al.*, 1994b).

Zein coatings have oxygen and carbon dioxide transmission rates that are lower by one or two orders of magnitude than those of low-density polyethylene (LDPE), methylcellulose (MC), and hydroxypropyl cellulose (HPC) films, and similar to those of polyester films at the same relative humidity (RH) and testing temperature (Krochta, 1992). Water vapor permeability (WVP) is satisfactory at low relative humidity, but increases rapidly as the RH increases. The importance of zein coatings in vegetables to enhance their shelf life is the way this limits their exposure to ambient oxygen and increases the internal carbon dioxide concentration (Park *et al.*, 1994a, 1994b).

Films

Zein films are easily cast from alcohol solutions. Zein is dissolved in warm (65–85°C) aqueous ethanol or isopropanol with added plasticizers. The solution is cooled to 40–50°C, allowing bubbling to cease prior to casting, and is then poured over a glass plate where a film is formed as the alcohol evaporates from the surface. The dried film is finally peeled off the plate (Gennadios *et al.*, 1993a).

Plasticizers are added to reduce film brittleness. They decrease the intermolecular forces between polymer chains, thus increasing flexibility and extendibility. The most common plasticizer for zein films is glycerol. However, it tends to migrate from the bulk of the film matrix to the food surface because its interaction with protein molecules is weak (Park *et al.*, 1994c). Cast zein films are initially transparent, but the glycerol “sweating out” causes a characteristic cloudiness, with a consequent loss in film flexibility (Park *et al.*, 1992). Mixtures of glycerol and polyethylene glycol (PEG) present slower migration rates of plasticizers than glycerol alone, but neither is effective at temperatures below freezing or in low relative humidity environments. Unsaturated fatty acids remain effective plasticizers in those conditions, but then lipid oxidation becomes an issue (Park *et al.*, 1994d; Lai and Padua, 1998).

The tensile properties of zein films are generally evaluated by two parameters; tensile strength (TS) and elongation at break (E). The TS of zein films is similar to that of wheat gluten films, and two- to threefold lower than that of MC and HPC films (Gennadios *et al.*, 1993a). In general, adding plasticizers decreases TS and increases E (Park *et al.*, 1994c). The TS of zein films varies substantially with RH and temperature conditioning, decreasing linearly with increase in RH and quadratically with temperature increase (Gennadios *et al.*, 1993a). TS increases up to twofold with the addition of cross-linking agents such as formaldehyde, glutaraldehyde or citric acid to the alcoholic film-forming solution (Yang *et al.*, 1996; Parris and Coffin, 1997).

Zein films have WVP values lower than or similar to those of other protein films, cellulose ethers, and cellophane (Krochta, 1992), but much higher than that of LPDE (Smith, 1986). Addition of plasticizers increases the WVP because of greater mobility of chain segments and subsequent greater diffusion coefficients of permeants (Seymour and Carraher, 1984). The WVP also increases with RH due to moisture plasticization and increasing vapor pressure differences between the two sides of the film (Lai and Padua, 1998). However, the low vapor-barrier ability of zein films could be considered an advantage, as it would allow excessive water vapor movement across the film, thus preventing water condensation inside the package leading to microbial spoilage (Ben-Yehoshua, 1985). Low WVP films require either treatment with cross-linking agents such as polymeric dialdehyde starch (PDS) (Parris and Coffin, 1997), or preparation of bilayer films (i.e. pouring, spraying or rolling a second film directly on top of a previously prepared one). Zein/soy protein and zein/wheat gluten films have lower permeability than single zein films (Foult and Bunn, 1994).

The oxygen and carbon dioxide permeabilities of zein films are lower than those of other polysaccharide and composite polysaccharide/lipid films (Greener and Fennema, 1989) but higher than those of wheat gluten films (Gennadios *et al.*, 1993b). Apparently, oxygen molecules can more readily permeate through the helical conformation of zein than through the highly cross-linked gluten structure. The oxygen permeability (OP) of zein films is also lower than that of common plastic films such as LPDE, propylene, polystyrene and polyvinyl chloride (Billing, 1989). The addition of plasticizers and increase in RH raise the OP (Yamada *et al.*, 1995) because moisture causes swelling of hydrophilic polymers, resulting in higher gas permeability (Ashley, 1985). Temperature affects the OP according to the characteristic Arrhenius activation energy model (Gennadios *et al.*, 1993b).

Zein may be plasticized in solution with long chain fatty acids, and collected as a soft solid mass after precipitation with cold water. Zein films may be drawn from wet, freshly precipitated resins after a kneading step, or formed by extrusion of dry resin pellets. Dry films are translucent, flexible, ductile, and heat-sealable. Under the microscope, they show a fiber network structure with pinholes and structural gaps (Padua and Wang, 2002). Fusion lamination, performed by heating several sheets together under pressure, produces transparent zein films that are more ductile and pliable than the original ones, filling pinholes and gaps in the structure and thus reducing macroscopic defects and increasing film uniformity (Rakotonirainy and Padua, 1999).

The TS and E values of drawn zein films are similar to those of cast films (Lai and Padua, 1997). Ductility increases at high RH due to the plasticization by moisture, resulting in higher E (Lai and Padua, 1998). Tensile properties of zein/fatty acid films are affected by fatty acid content. For example, increasing oleic acid from 0.5 to 1.0 g/g zein decreases the TS and increases E (Santosa and Padua, 1999).

Drawn zein films have a lower equilibrium moisture content (7 g water/100 g solids) than cast zein films of identical composition (12 g water/100 g solids) at a water activity value of 0.95, owing to more extensive zein–fatty acid interactions, which cause a reduction on zein exposure to water (Lai and Padua, 1998). The WVP is relatively low compared to that of hydrophilic biopolymers such as wheat gluten (Park and Chinnan, 1990) and cellophane (Taylor, 1986), but is at least one order of magnitude higher than that of LPDE films (Smith, 1986). Expectedly, WVP increases at higher RH and temperatures (Lai and Padua, 1998). Coating drawn-zein films with tung or linseed oils reduces the WVP by up to tenfold (Rakotonirainy and Padua, 1999).

Morphological differences are clear between cast and drawn films plasticized with oleic acid. Cast films show a different finish on their two sides; the side in contact with the casting surface is smooth and glossy, while the one in contact with air during drying is irregular and opaque. In contrast, both drawn-film surfaces are smooth and low gloss. Scanning electron microscopy reveals that the glossy sides of cast films are featureless, whereas the opaque sides show globular deposits due to fatty acids separated from the zein matrix by the evaporating solvent. Thermograms also suggest a more extensive interaction between zein and fatty acids in drawn films than in cast films (Lai and Padua, 1997).

Applications

The potential increase in zein availability has activated research on its properties and utilization. Although presently pharmaceutical coating and confectionery glazing form the bulk of zein commercial applications, intensive research on zein utilization for edible and biodegradable film formulations has resulted in improved performance. Plasticization with polyols and fatty acids reduces stiffness and increases film flexibility, while heat treatment under high pressure improves clarity and texture. Coating with water-resistant lipids reduces WVP and permits exposure to high RH environments. There are even attempts to scale film production by extrusion. The main challenge is to modify the mechanical properties of films produced by the present methods, which

increase TS, resulting in higher stiffness and reduced flexibility (Padua and Wang, 2002). As zein films present very important advantages as biodegradable packaging materials for their resistance to rodent and insect attack and freezing and thawing cycles, it is expected that there will be advances in improving their properties, thus allowing commercial applications in the near future.

Soy protein films

Soy protein used in the food industry is classified as soy flour, concentrate or isolate, based on the protein content. Defatted soy flour (DSF) contains 50–59% protein, and is obtained by grinding defatted soy flakes. Soy protein concentrate (SPC) contains 65–72% protein, and is obtained by aqueous liquid extraction or acid leaching processes. Soy protein isolate (SPI) contains more than 90% protein, and is obtained by aqueous or mild alkali extraction followed by isoelectric precipitation (S. K. Park *et al.*, 2002). Soy protein is a viable and renewable resource for producing edible and environmentally friendly biodegradable films. The use of soy protein as a film-forming agent can add value to soybeans by creating new channels for marketing soy protein, in particular SPI, which is of low cost and plentiful supply and is actually an under-utilized product despite its high protein quality (Raynes *et al.*, 2000).

Formation of soy protein films

Soy protein films are typically prepared from SPI by drying thin layers of cast film-forming solutions (Subirade *et al.*, 1998). The drying temperature and RH that determine the drying rate of cast solutions can also affect the film structure and properties. Rapid drying at 95°C and 30% RH yields films that are stronger, thinner, stiffer, and less extendable than films dried more slowly at 21°C and 50% RH. Also, the former have lower WVP than the latter (Alcantara *et al.*, 1998). Soy protein films need the addition of plasticizers for texture and flexibility, and glycerol and sorbitol are the ones most commonly used (Gennadios *et al.*, 1994).

Extruding soy protein formulations into films is also possible, using SPI, plasticizer, and water as the main formulation ingredients (Naga *et al.*, 1996). Films have also been extruded from blends of SPI, polyethylene oxide, and LDPE (Ghorpade and Hanna, 1996). *Yuba*, a Japanese word for soymilk film, is the dried film formed on the surface of heated soymilk at temperatures close to the boiling point (Wu and Bates, 1972; Sian and Ishak, 1990; Gennadios and Weller, 1991). Soy protein polymerization is attributed to disulfide bonds and, to a lesser degree, hydrophobic interactions and hydrogen bonds. Dried yuba is quite brittle, has a relatively long shelf life, and is used as a wrapper for other foods, is cooked with other foods, or is used in soups (Liu, 1997).

Functional properties of soy protein films

In general, soy protein films have poor moisture resistance and water vapor barrier ability due to the inherent hydrophilicity of the protein and the substantial amounts of

hydrophilic plasticizers used to impart film flexibility (Rhim *et al.*, 2000). Compared to LDPE films, cast SPI films have greater WVP values by roughly four orders of magnitude (Gennadios *et al.*, 1993c). In contrast, soy protein films are potent oxygen barriers, at least at low RH environments (Gennadios *et al.*, 1993b; Ghorpade *et al.*, 1995).

In the case of SPI films, mechanical properties depend on the development of disulfide bonds, hydrophobic interactions and hydrogen bonds within the protein matrix. Interactions between proteins and small molecules, including water, plasticizers, lipids, and other additives dispersed in the space of the matrix, also contribute to the mechanical behavior of protein films (Chen, 1995). In general, soy protein films, similar to films from other proteins, have only moderate mechanical properties compared to commonly used plastic films such as polyethylene, polypropylene, and polyvinylidene chloride (Gennadios *et al.*, 1994; Krochta and De Mulder-Johnston, 1997).

Heating above 60°C and alkaline conditions below pH 10.5 promote soy protein polymerization by altering the three-dimensional structure through the unfolding of polypeptide chains, thus exposing sulfhydryl and hydrophobic groups (Kelley and Pressey, 1966). The alkaline conditions also favor thiol-disulfide interchange reactions by deprotonating sulfhydryl groups and allowing them to act as nucleophiles. Upon drying the cast solutions, unfolded macromolecules approach each other and are linked by disulfide bonds and hydrophobic interactions. SPI films from solutions heated at 95°C have greater TS and E values than films from solutions heated at 75°C (Park and Hettiarachchy, 2000).

Protein-film formation is also pH dependent. SPI films can be formed in both alkaline and acidic conditions. In a study of interfacial film formation, lipids (corn oil or glycerol trioleate) were added to SPI solutions and satisfactory films were produced at pH values lower than 4.6 (as low as pH 1), the isoelectric region of soy protein, and as high as pH 6.5. Above pH 7.4, the increasing solubility of SPI limited film formation (Flint and Johnson, 1981). Cast films formed in alkaline conditions have been reported to have greater TS and E and lower WVP than films formed in acidic conditions. Similar to heating, alkaline conditions facilitate soy protein denaturation, thus promoting the formation of disulfide bonds within the structure of the dried films (Gennadios *et al.*, 1993c).

Besides heating soy protein film-forming solutions prior to casting, cast SPI films have also been subjected to heat treatments (heat curing) to modify their properties. For example, heating SPI films at 80 or 95°C for 2, 6, 14 or 24 hours increased TS and reduced E, WVP and water solubility (Gennadios *et al.*, 1996). In general, thermal treatments of proteins promote the formation of intra and intermolecular cross-links, mainly involving lysine and cystine amino acid residues (Cheftel *et al.*, 1985). The increased cross-linking within the protein network directly affects film properties (e.g. increased TS and reduced E). Moreover, this heat-induced cross-linking probably involves the reactions among polar protein groups, thus enhancing film hydrophobicity. For example, SPI films heat-cured in an air-circulating oven at 90°C for 24 hours had a lower moisture content than untreated SPI films after conditioning at 50% RH and 25°C for 2 days (Rhim *et al.*, 2000). Because water has a plasticizing effect on protein-based films, the decreased moisture content of heat-cured films likely contributes further to their increased mechanical toughness (Gontard *et al.*, 1993).

The use of enzymes that promote protein cross-linking to improve protein film properties appears feasible. Horseradish peroxidase has been used for such purposes. This enzyme catalyzes the oxidation of tyrosine residues, forming di-, tri- and tetra-tyrosine. Incubating SPI film-forming solutions with this enzyme at 37°C for 24 hours does not affect WVP but increases TS and protein solubility, and decreases E. Because of the increase in protein solubility, it is assumed that horseradish peroxidase causes protein degradation in addition to cross-linking (Stuchell and Krochta, 1994).

The ability of low molecular weight aldehydes such as formaldehyde to react with primary amino groups and sulfhydryl groups in proteins, thereby forming intra- and intermolecular crosslinks, is well documented (Feeney *et al.*, 1975). Formaldehyde can be directly added to SPI film-forming solutions, or it can be applied by immersing dried SPI films into formaldehyde solutions (Rhim *et al.*, 2000). Treatment with formaldehyde results in larger than twofold increases in TS and puncture strength (PS), while also reducing WVP by about 6% and water solubility by about 42% (Ghorpade *et al.*, 1995). However, aldehydes are generally toxic and non-edible, which limits their possible use to non-edible applications (S. K. Park *et al.*, 2002).

Reportedly, aromatic amino acids such as tyrosine and phenylalanine are able to absorb UV light and recombine to form covalent cross-links in proteins (Tomihata *et al.*, 1992). Subjecting cast SPI films to UV irradiation increases TS and decreases E, although WVP is not affected (Gennadios *et al.*, 1998a).

The water-barrier capability of protein films can be improved through combination with hydrophobic lipid materials (Gennadios *et al.*, 1994; Krochta and De Mulder-Johnston, 1997). One approach is to add the lipids to protein film-forming solutions, which are then cast to prepare emulsified, bi-layered or multi-component films. Alternatively, molten lipids can be deposited (laminated) onto preformed protein films to prepare multi-layered composite films. For example, the addition of fatty acids (i.e. lauric, myristic, palmitic, oleic) to SPI film-forming solutions caused a substantial decrease in WVP as well as a plasticizing effect translated into a much higher E (228% versus 70% in the control). However, because lipids lack the structural integrity of proteins or polysaccharides, the addition of fatty acids greatly reduces TS (Gennadios *et al.*, 1998b). Another concern regarding protein-lipid films is their potential susceptibility to lipid oxidation.

The formation of covalent cross-links between proteins and propylene glycol alginate (PGA) has been documented (McKay *et al.*, 1985). The ϵ -amino groups of lysine are involved in soy protein interaction with PGA. SPI-PGA films prepared with low levels of PGA (10% w/w of protein) have increased TS and water resistance (Shih, 1994; Rhim *et al.*, 1999). Although PGA is edible, its use as a cross-linker for protein films would reduce the nutritional value of protein by impairing the availability of lysine. Nevertheless, an edible film or coating is unlikely to contribute notably to the nutritional content of foods (S. K. Park *et al.*, 2002).

As aforementioned, soy protein films are formed through polymerization of heat-denatured proteins, disulfide bonds and hydrophobic interactions being the main forces that maintain the film network (Shimada and Cheftel, 1998). In sulfur-containing protein systems such as SPI, cysteine groups can undergo polymerization via sulfhydryl-disulfide interchange reactions during heating to form a continuous covalent network

upon cooling (Arntfield *et al.*, 1991). For example, addition of cysteine (1% w/w) to SPI film-forming solutions at pH 7 increased the number of disulfide bonds in the solutions by 576.6%, and also increased the TS of cast films (Were *et al.*, 1999).

Applications

The high oxygen-barrier capability of SPI films could be utilized in the manufacture of multi-layer packaging where protein films would function as the oxygen barrier-providing layer. SPI coating on precooked meat products could control lipid oxidation and limit surface moisture loss. Incorporation of antioxidants and flavoring agents in SPI coatings could improve the overall quality characteristics of food products (Kunte *et al.*, 1997). Also, SPI films may find applications as microencapsulating agents of flavors and pharmaceuticals, or in coatings of fruits, vegetables, and cheese (Petersen *et al.*, 1999). Protective SPI coatings could also be used on certain food products, such as meat pies and high-moisture-low-sugar cakes, which require films that are highly permeable to water vapor (Gennadios *et al.*, 1993b).

Wheat gluten films

The very high molecular weight, markedly apolar character, complexity, and diversity of their fractions are features of wheat gluten (WG) proteins that can be utilized to make films with novel functional properties, such as selective gas-barrier properties and rubber-like mechanical properties. WG-based materials are homogeneous, transparent, mechanically strong, and relatively water resistant. They are biodegradable, biocompatible, and edible when food-grade additives are used (Guilbert *et al.*, 2002).

Vital WG is the cohesive and elastic mass that is left over after starch is washed away from wheat flour dough. Commercially, it is an industrial by-product of wheat starch production via wet milling. Whereas dry wheat flour comprises 9–13% protein and 75–80% starch, WG consists mainly of wheat storage protein (70–80% dry matter basis) with traces of starch and non-starch polysaccharides (10–14%), lipids (6–8%), and minerals (0.8–1.4%). WG is suitable for numerous food and non-food uses. Its main application is in the bakery industry, where it is used to strengthen weak flours, rendering them suitable for bread baking. It is widely accepted that the unique rheological properties of WG are derived from its protein composition, with lipids and carbohydrates being contaminants entangled in the protein matrix (Guilbert *et al.*, 2002).

There are four wheat-protein classes, based on solubility in different solvents, namely albumins, globulins, gliadins, and glutenins. The albumins and globulins (15–22% of total protein), which are water and saline soluble respectively, are removed with starch granules during gluten separation processing. In contrast, gliadins (prolamins), which are soluble in alcohol, and the glutenins, which are soluble in dilute acid or alkali solutions, are collected into gluten. Gliadins and glutenins amount to up to 85% (w/w) of total wheat flour protein, and are evenly distributed into gluten (Wrigley and Bietz,

1988). Gliadin is named prolamins due to its large proline and glutamine content. The solubility of gliadin in 60–70% alcohol results from its peculiar amino acid composition (Lafiandra and Kasarda, 1985). In the fully hydrated state, gliadin exhibits viscous flow properties without significant elasticity. For cereal technologists, gliadin accounts for the extensibility of wheat flour dough, also acting as a filler by diluting glutenin interactions (Guilbert *et al.*, 2002). Glutenin has a similar amino acid composition to gliadin, with a slightly lower content of hydrophobic amino acids (Wrigley and Bietz, 1988). Contrary to gliadin, which is comprised of distinct polypeptide chains, glutenin consists of polymers made from polypeptide chains (also named subunits) linked end-to-tail by disulfide bonds. Glutenin is believed to be one of the largest natural polymeric molecules, with an estimated molecular mass of well over 10^7 (Kasarda, 1999).

Formation of wheat gluten films

Film formation from WG solutions or dispersions has been extensively studied (Gennadios and Weller, 1990; Gennadios *et al.*, 1993b, 1993c, 1993d, 1993e; Park and Chinnan, 1995). WG films can be obtained by casting from solution or by extrusion, the latter being more cost effective. WG films have also been produced by collecting the surface skin formed during the heating of WG solutions to temperatures near boiling (Watanabe and Okamoto, 1976).

WG proteins are insoluble in water, and require a complex solvent system with basic or acidic conditions in the presence of alcohol and disulfide bond-reducing agents. Generally, changing the pH of the medium disrupts hydrogen and ionic interactions, while ethanol disrupts hydrophobic interactions (mainly occurring among gliadin molecules). Intermolecular (for glutenins) and intramolecular (for gliadins and glutenins) covalent disulfide bonds are cleaved and reduced to sulfhydryl groups when dispersing WG in alkaline environments (Okamoto, 1978). Reducing agents, such as sodium sulfite, cysteine or β -mercaptoethanol, should be used in acidic environments to destroy disulfide bonds. A wide variety of acids can be used, including citric, acetic, phosphoric, propionic, and lactic acids. On the other hand, bases such as sodium hydroxide, potassium hydroxide, and (mainly for its volatility) ammonium hydroxide are used to reduce disulfide bonds (Guilbert *et al.*, 2002).

During drying, all these volatile disruptive agents are progressively eliminated. Solvent removal increases the concentration of WG proteins. Consequently, active sites for bond formation become free, and are close enough to each other to create new interactions. New hydrogen bonds, hydrophobic interactions, and disulfide bonds contribute to the formation of a three-dimensional network. Solvent removal can be fractionated to obtain film-forming solutions with a very low alcohol concentration (Guilbert *et al.*, 2002).

The addition of plasticizers is essential to avoid film brittleness as a consequence of extensive intermolecular associations. Sorbitol, manitol, diglycerol, propylene glycol, triethylene glycol, maltitol, polyvinyl alcohol, and PEG are used as plasticizers for WG films, but glycerol and ethanolamine are preferred. These molecules are small enough to insert themselves between the protein chains, and to form hydrogen bonds

through their hydroxyl groups. In terms of level of use, plasticizers are employed in amounts sufficient to lower the glass transition temperature to the ambient temperature. Typical plasticizer levels are 15–40% of protein weight (preferably 20–30%). Polar plasticizers increase the hygroscopicity of WG-based materials. In addition, they diffuse out easily if the material is in contact with a moisture-rich product. For these reasons, the research for non-polar, low-diffusivity plasticizers is essential for the development of WG-based plastics. The use of amphiphilic plasticizers, such as fatty acids and derivatives, should be recommended (Gennadios *et al.*, 1993b, 1993c, 1993d, 1993e; Park and Chinnan, 1995; Guilbert *et al.*, 2002).

Extrusion for WG-film formation is a thermoplastic process involving a thermal treatment with glass transition followed by a thermoforming step. Extrusion of plasticized WG has been performed using a co-rotating, intermeshing twin-screw extruder (Redl *et al.*, 1999).

Functional properties of wheat gluten-based films

Cohesion of WG-based materials depends mainly on the type and density of intra- and intermolecular interactions, but also results from interactions with other constituents. WG films show low TS but high E compared to other films (Gennadios *et al.*, 1993c). The mechanical properties of WG films depend greatly on processing conditions, the addition of plasticizers, lipids, and cross-linking agents, and external conditions such as RH and temperature. Glycerol and water act as plasticizers of WG films, generally reducing mechanical resistance and increasing extensibility. However, at a very low water content and thus low RH (below 15 g/100 g dry matter and 60%, respectively), hydration has a positive effect on film mechanical resistance, probably due to formation of supplementary hydrogen bonds among protein chains (Gontard *et al.*, 1993). Increasing the processing temperature from 80 to 135°C induces an increase in mechanical resistance of the WG network and a decrease in elongation (Cuq *et al.*, 2000).

The WVP of WG films is equivalent to that of other protein- or polysaccharide-based films, but is relatively high compared to that of synthetic polymer films. The WVP through WG films increases with increasing RH and temperature – for example, at 30°C the WVP is tenfold lower at 50% RH than at 93% RH. The WVP of WG films is also highly dependent on the nature and amount of the added plasticizer. A linear relationship exists between the glycerol concentration and WVP of WG films (Gontard *et al.*, 1993).

Similar to WVP, the oxygen, carbon dioxide, and ethylene permeabilities of WG films are highly dependent on RH and temperature. At low RH and temperature a WG film has very low oxygen and carbon dioxide permeabilities compared to other biopolymer or synthetic polymer films. For example, at 0% RH the oxygen permeability of a WG film was found 800-fold lower than that of LDPE and 9.6-fold lower than that of polyamide-6 (a well-known potent oxygen-barrier polymer at 0% RH). Also, the WG film was 2.6- and 570-fold less permeable to carbon dioxide than are polyamide-6 and LPDE, respectively. Interesting applications of WG films as oxygen and carbon dioxide barriers in dry conditions could thus be considered (e.g. for low water activity products, or sandwiched between two layers of a highly water-resistant material) (Billing, 1989). However, the gas permeability values of WG films increase substantially with

increasing RH and temperature in an almost exponential fashion above 50% RH (Mujica-Paz and Gontard, 1997). Increased RH promotes both gas diffusivity (due to the increased mobility of hydrophilic macromolecular chains) and gas solubility (due to swelling of the matrix by absorbed water), leading to a sharp increase in gas permeability. With carbon dioxide, the sharp increase of permeability is more pronounced than with oxygen. The effect of RH on gas permeability also varies with temperature, following (approximately) the Arrhenius model (Gontard *et al.*, 1996).

It is also possible to combine WG with other materials in order to optimize film properties. Films made from WG and lipids can combine the water vapor resistance of the lipids with the relatively good mechanical properties of the WG. Lipids can either be incorporated in WG-film-forming solutions to obtain composite films (emulsion technique) or deposited as a layer onto the surface of preformed WG films to obtain bi-layer films (coating technique). The effects of lipids incorporated into WG film-forming solutions can vary from destruction of the protein network to improvement of the mechanical and barrier properties of the cast films. These effects are complex, and are dependent on the nature and structure of the lipids and on the chemical interactions between the lipids and the protein. For example, combining WG with a diacetyl tartaric ester of monoglycerides at 20% w/w dry matter produced films that, when compared to the control glycerol-plasticized WG films, were as transparent, had higher mechanical resistance, and had about 50% lower WVP. However, improving the moisture-barrier properties of such composite films by increasing lipid concentration has proved to be of limited value because the hydrophilic protein matrix alters the resistance of the lipid components to WVP (Gontard, 1991). The coating technique for preparing bi- or multi-layer WG-lipid films has shown opposite results in the literature, with some studies reporting the process to be more effective than the emulsion technique (Gontard *et al.*, 1995) and others reporting it to be less effective (Koelsch, 1994).

There have been studies in which bi-layer films composed of a WG film and a modified PE film were prepared, thus combining the gas selectivity of the WG films with the excellent mechanical properties and moisture resistance of the PE films. WG films were prepared first using a casting procedure and then hot-pressed with the PE films at different temperatures. The TS and E values of bi-layer films made of polyethylene maleic anhydride (PGMA) and WG were not affected by RH, unlike those of WG films. Also, the gas and water vapor permeability values of the PGMA-WG films were considerably reduced as compared to those of control WG films (Pérez-Pérez, 1997).

Post-production treatments of wheat gluten films

WG films are relatively water resistant and water insoluble, but their high WVP due to their inherent hydrophilic nature remains the greatest limitation for their use (Gennadios *et al.*, 1993d). Furthermore, their mechanical and water vapor barrier properties are strongly affected by water or other plasticizers (Gontard *et al.*, 1993). The functional properties of WG-based films can also be improved by subjecting the film-forming solutions to various treatments prior to casting. Such treatments can be enzymatic, chemical, thermal or radiative (Gennadios and Weller, 1990; Gontard *et al.*, 1993; Herald *et al.*, 1995).

Heat treatments promote protein aggregation through disulfide bonding and hydrophobic interactions (Gennadios *et al.*, 1996; Ali *et al.*, 1997; Cuq *et al.*, 2000; Micard and Guilbert, 2000). This may be responsible for the observed changes in the mechanical and barrier properties of heat-treated protein films. Heat curing of WG films increases TS and decreases E. For example, the TS and E of cast films heated at 140°C reached up to 300% and 43%, respectively, of the value obtained when the films were heated at 80°C. The WVP of WG films at 25°C and 60% RH decreases as the exposure time increases at a given temperature. WG films appear to be rather sensitive to color changes following heat curing, particularly with regard to yellowness.

Formaldehyde is the main chemical that has been used to treat preformed protein films. It leads to a drastic insolubilization of proteins by reinforcing the protein network through covalent linkages. Both soaking (Guéguen *et al.*, 1998) and vapor exposure (Micard and Guilbert, 2000) have been used to apply formaldehyde to protein films, the latter approach offering more reproducible results. Such exposure increased TS and stiffness by 400% and decreased E by 62%, although no significant changes in WVP were observed (Micard and Guilbert, 2000). Immersion of cast WG films in calcium chloride or buffer solutions at the isoelectric point of WG (pH 7.5) increased TS by 46% and WVP by about 15%. No changes were observed with regard to OP (Gennadios *et al.*, 1993e).

Gamma radiation increases TS (43%) and stiffness (79%) and decreases E (32%) of WG films. This effect is explained by the formation of dityrosine cross-linkages within polypeptide macromolecules. The WVP increases as well (19%), probably because of glutenin degradation (Micard and Guilbert, 2000).

Aging WG films at 20°C and 60% RH for 360 hours increases TS (75%) and stiffness (314%) and decreases E (36%) in comparison to similar conditions of aging over 48 hours. No significant changes are observed with respect to WVP (Morel *et al.*, 2000).

Applications

Application of WG-based materials can be envisioned for the coating of seeds, pills, and foodstuffs, and for making cosmetic masks, polishes or drug capsules. It is important to note that the allergenic character of WG-based products for people suffering from celiac disease could limit such applications to cereal-based products in which the presence of WG or similar cereal proteins is known and expected. The moisture-, gas-, and solute-barrier properties of WG-based films could be particularly interesting for applications in the fields of active coatings, active packaging, drug delivery systems, and modified atmosphere packaging (Guilbert *et al.*, 2002).

Cottonseed protein films

Cotton is a plant that has been cultivated in 70 different countries for centuries as a fiber crop. Cottonseed accounts for about 13% of world oilseed production, although

oil production accounts only for about 15% of the commercial value of the cottonseed crop. To optimize the usage of this low-cost, oil-rich, and protein-rich commodity, the film-forming properties of cottonseed proteins could be used to produce biodegradable materials of economic and environmental interests (Wu and Bates, 1973; Marquié *et al.*, 1996, 1997a, 1997b).

Cottonseed is crushed to extract oil and to produce cake that is chiefly used for ruminant livestock (Tacher *et al.*, 1985; Zongo and Coulibaly, 1993). As it contains gossypol, a toxic compound, this cake cannot be used for human consumption. Cottonseed proteins make up 30–40% w/w of the cottonseed kernel. Other important cottonseed components include lipids, soluble carbohydrates, cellulose, minerals, phytates, and polyphenolic pigments. The protein components are mainly globulins (60%) and albumins (30%), with much lower proportions of prolamins (8.6%) and glutelins (0.5%) (Saroso, 1989).

Cottonseed proteins have a high content of ionizable amino acids (aspartic and glutamic acids, arginine, histidine and lysine) and a low content of sulfur amino acids. These proteins are more soluble at a basic pH than at an acidic pH, and have an isoelectric point of around 5 (Bérot and Guéguen, 1985; Dumay *et al.*, 1986). Cottonseed proteins are readily denatured by thermal treatment above 80°C, leading to loss of solubility and nutritional value (Besançon *et al.*, 1985). The temperature increase during the crushing of cottonseed induces chemical interactions between gossypol and lysine, and also Maillard reactions (Marquié, 1987; Bourély, 1990).

Formation of cottonseed films

Initially, cottonseed films were prepared by soaking cottonseed kernels in hot water to prepare an “oilseed milk” from which films were formed on the surface of the heated liquid, similarly to traditional yuba (soy protein) films in East Asia (Wu and Bates, 1973). Owing to their poor mechanical properties, films made with this process may be used as edible items but not as packaging materials.

Cottonseed protein-based films are obtained directly from cottonseed flour using a casting process (Marquié, 1995, 1996; Marquié *et al.*, 1995, 1997a, 1997b, 1998). The first step involves solubilizing cottonseed flour proteins under appropriate conditions (solvent, pH, and temperature, and the addition of salts, plasticizers, and dissociating agents) to minimize protein–protein interactions. Changes in the protein structure prevent “remelting” of macromolecules and reveal potentially interactive zones. The dispersions are then centrifuged to remove insoluble substances, and the supernatants are homogenized. Glycerol is added as a plasticizer to the film-forming solution. Drying allows solvent removal and the formation of three-dimensional protein networks through new inter- and intramolecular linkages.

In contrast to protein isolates, the conditions required to obtain films from cottonseed flour-based solutions are difficult to determine because of the complex nature of the raw material, which contains proteins, lipids, ash, cellulose, and carbohydrates. The following general ranges have been established for cottonseed flour film formation: pH 8–12, temperature 20–60°C, solid/solvent ratio 10–50% w/v, use of dispersing agents and plasticizer content (10–50% w/w, dry basis). Films containing lipids

are weaker than those made from defatted flour; this is explained by the protein content, which is evidently lower in lipoprotein films than in films made from delipidated flour. The presence of gossypol leads to less soluble films. The film color varies from light yellow (in the absence of gossypol) to brown (in the presence of gossypol). Films from defatted cottonseed flour are smooth and transparent.

Cottonseed flour films are excessively brittle when the glycerol content is below 10% w/w dry basis, and become sticky when glycerol content is higher than 30% (Marquié *et al.*, 1995). Glycerol decreases the intermolecular forces between polymer chains, with a decrease in cohesion, tensile strength, and glass transition temperature (Guilbert, 1986). Gossypol is characteristically oxidized into quinones at an alkaline pH, forming Schiff bases with ϵ -amino groups of lysine. In protein films, gossypol strengthens the protein network (Tchiegang and Bourély, 1990; Marquié *et al.*, 1995).

Films can be strengthened by cross-linking agents able to modify proteins chemically during the preparation of film-forming solutions. The main cross-linking agent for cottonseed protein is formaldehyde. In alkaline solution, formaldehyde forms short methylene cross-links between lysine amino groups (Means and Feeney, 1968; Bizzini and Raymund, 1974). Chemical treatment of cottonseed proteins with formaldehyde, using a formaldehyde-lysine reactive mix in the film-forming solution, produces films with a greater puncture strength (PS) than when using other cross-linking agents such as glyoxal or glutaraldehyde (Marquié, 1996).

It is also possible to incorporate carded cotton fibers into cottonseed flour films and plastic-like materials. The resulting films resemble bi-layer films in combining the properties of each polymer component (cellulose and protein). For example, plastic-like materials with proteins that were cross-linked by glutaraldehyde and contained 8% carded cotton fibers (w/w, dry basis) were five times more water resistant (Marquié *et al.*, 1996).

Functional properties of cottonseed flour-based films

Films from cottonseed flour are highly hydrophilic owing to their protein content and protein composition (Gontard *et al.*, 1993; Gennadios and Weller, 1994). Their mechanical properties are affected by both temperature and RH. Water acts as a plasticizer in cottonseed flour films by increasing the molecular mobility in the protein network and decreasing the apparent glass transition temperature at which film mechanical properties change (Marquié, 1996).

The PS of cottonseed flour films varies as a function of film moisture content and water activity. At low water activity (0.1), films with low moisture content (2–3% w/w, dry basis) are very brittle. PS then increases sharply for film moisture contents within 3–7% (w/w, dry basis). The increase in film PS at low water content may be interpreted as an antiplasticizing effect of water (Guo, 1994a, 1994b). At film moisture contents up to 7% (w/w, dry basis), water plasticizes the film structure through extensive hydrogen bonding among protein chains, thus increasing molecular mobility with a concomitant decrease in PS. The TS of cottonseed flour films, even cross-linked with formaldehyde, is five- to tenfold weaker than films made from synthetic materials;

however, cottonseed flour films that contain cotton fibers are as strong as them. The WVP of cottonseed flour films compares to that of other protein films such as SPI or zein, but is about 100-fold higher than that of polyethylene (Marquié, 1996).

Applications

Cottonseed flour films may be suitable for certain applications in non-food packaging (e.g. compostable waste bags) where good mechanical resistance and insolubility in water are required. They can also be used for agricultural packaging and mulching films to protect crops and fixate seeds, and other applications where film color, porosity, and biodegradability are beneficial (Marquié and Guilbert, 2002). They could be used in certain medical areas where biodegradability is necessary (e.g. prostheses and resorbable dressings). The ability of these films to absorb considerable amounts of moisture is a further advantage for exudate absorption (Marquié, 1995). It should be also possible during film preparation to introduce active compounds (e.g. insecticides, fungicides and bactericides) that could migrate out of the films and offer a specific environmental action. Film hydration, accompanied by increased WVP and diffusion of small molecules, would make these materials suitable vectors for active substances in delicate environments (Marquié and Guilbert, 2002).

Other protein films

Corn, soybean, wheat, and cottonseed are the prevalent types of plant from which proteins with film-forming ability are obtained. Nevertheless there are other plant proteins, of limited availability, that may be of interest, due to a unique property they provide to films or an advantage with regard to film formation. Limited availability may be because of relatively low production of the protein source or limitations in recovering the protein as a co-product from a process. The nature, recovery, film formation and film properties of protein obtained from peanut, rice, pea, pistachio, and grain sorghum are discussed here (H. J. Park *et al.*, 2002).

Peanut protein

Peanut protein concentrates (PPC) and isolates (PPI) are commercially produced from defatted peanut flour using several methods. Hydraulic pressing, screw pressing, solvent extraction, and pre-pressing followed by solvent extraction have been used for defatting (Natarajan, 1980; Woodroof, 1983). After oil removal, protein isolation and purification are necessary. Peanut concentrates (about 70% protein) are produced from dehulled kernels by removing most of the oil and the water-soluble, non-protein components. Techniques for removing water-soluble components include water leaching at the isoelectric pH, aqueous alcohol leaching, air classification, liquid cyclone fractionation, and moist heat denaturation followed by water leaching. PPI (about

90–95% protein) are produced by further processing of PPC to remove water-insoluble oligosaccharides and polysaccharides, and other minor constituents (Natarajan, 1980). Peanut proteins are deficient in methionine, lysine, and, possibly, threonine and tryptophan. In addition, there is a proven allergenicity associated with peanut proteins. These limitations must be considered when peanut proteins are added to foods for nutritional purposes (Natarajan, 1980).

Two different methods have been used to prepare peanut-protein films. The first method involves the formation of peanut-protein–lipid films on the surface of heated peanut milk (Wu and Bates, 1973; Aboagye and Stanley, 1985; Del Rosario *et al.*, 1992). This film production is similar to that of the traditional Asian *yuba*. The second method involves casting of PPC or PPI solutions. For example, films were prepared from PPC solutions adjusted to pH 6.0, 7.5 or 9.0, and dried at 70, 80 or 90°C. Glycerin, sorbitol, PEG or propylene glycol were added as plasticizers. Films formed at a higher pH (7.5 or 9.0) and higher drying temperature (80 or 90°C) were less moist and sticky at the surface than films formed at pH 6.0 and a drying temperature of 70°C. Glycerin was determined to be the best performing plasticizer. Increasing the film-drying temperature decreased the WVP, but increasing the pH had no effect, and it was hypothesized that the reduction of WVP with increased drying temperature was due to greater cross-linking, resulting in a tight and compact protein film structure. The effects of pH and drying temperature on OP were similar to those on WVP. TS and E increased when film-drying temperature increased from 70 to 90°C. This was attributed to increased protein denaturation at the higher temperature, which also likely resulted in a tighter, more compact film structure (Jangchud and Chinnan, 1999a, 1999b).

Rice protein

Abrasive milling removes the outer tissue material from rice kernels, producing polished rice and the side products of bran and polish. Usually, 10% by weight of brown rice is removed during milling. Bran accounts for 5–8% of the rough rice weight, and polish accounts for a further 2–3%. Rice bran and polish contain 12.0–15.6% and 11.8–13.0% protein, respectively (Houston, 1972). Rice bran protein concentrates are prepared from commercially available unstabilized or heat-stabilized rice bran by alkaline extraction and isoelectric precipitation (Gnanasambandam and Hettiarachchy, 1995). Rice protein concentrate can be prepared by alkaline extraction of rice flour or of broken rice kernels, a side-product of rice milling. Alternatively, rice flour or kernels may be treated with enzymes to partially remove the starch component (Chen and Chang, 1984).

Films from rice bran protein solutions (70% protein, dry basis) have been prepared using glycerol as a plasticizer (2% w/v), adjusting the pH to either 9.5 or 3.0, heated to 80°C, poured onto polyethylene plates and dried at 60°C (Gnanasambandam *et al.*, 1997). Films prepared at pH 9.5 resulted in darker (a more intense reddish-yellow tan color) and more transparent films than those prepared at pH 3.0. No substantial differences were observed with regard to WVP between films prepared at pH 3.0 and 9.5. Rice bran films have higher WVP than synthetic films because of the hydrophilic nature of the protein – the majority of proteins in rice bran are albumins and globulins.

OP was affected by pH, with films prepared at pH 3.0 showing lower values than films prepared at pH 9.5. The lower solubility of rice bran protein at pH 3.0 may result in a tighter film structure and, thus, reduced OP. PS was greater for rice bran protein films prepared at pH 9.5 than for those prepared at pH 3.0. Rice bran proteins were less soluble at pH 3.0, resulting in fewer protein–protein interactions and hence lower PS than films prepared at pH 9.5. The TS showed a similar trend with pH changing from the basic to the acid region (Gnanasambandam *et al.*, 1997).

Pea protein

Pea proteins are separated from starch and fiber by multi-step solubilization at pH 2.5–3.0, followed by centrifugation (Nickel, 1981). These protein isolates have a mean crude protein content of 85.3% and an ash content of 4.1–5.0%. They show a lower fat absorption than SPI, suggesting the presence of more numerous hydrophilic than hydrophobic groups on the surface of protein molecules (Nackz *et al.*, 1986). Pea protein consists primarily of globulins (>80% of total protein) and a small fraction of albumins. The globulins are storage proteins located in the cotyledons, whereas albumins are cytoplasmic proteins consisting of many different subunits (Boulter, 1983; Mosse and Pernollet, 1983). Pea protein possesses good nutritional quality (i.e. protein efficiency ratio and essential amino acid content) and has potential as a dietary protein fortifier (Linden, 1985), although a relatively poor functionality has been reported with respect to protein solubility, emulsion stability, and gelation characteristics (Sumner *et al.*, 1981; Jackman and Yada, 1989).

Owing to their globular structure, pea proteins need unfolding under alkaline conditions prior to film formation. An industrial pea protein concentrate (70.6% protein) has been utilized to cast films plasticized with various polyols (e.g. mono-, di-, tri- and tetra-ethylene glycol, glycerol and propane diol) and dried at 60°C. Glycerol-plasticized pea-protein films are sticky, while propane diol-plasticized films become brittle rapidly. Ethylene glycol gives films of greater TS and E, and lower WVP, than di-, tri- or tetra-ethylene glycol. Overall, pea-protein isolate films show lower TS and E, and greater WVP (by one or two orders of magnitude), than LPDE. Cross-linking with formaldehyde substantially reduces the water solubility and increases the TS of these films – an expected effect due to the high lysine content of pea protein (Guéguen *et al.*, 1995, 1998).

Films made from denatured pea-protein isolate (*ca.* 85% protein) show physical and mechanical properties similar to those of soy protein and whey protein films, and possess the strength and elasticity to resist handling. Increasing the concentration of glycerol as a plasticizer in the film decreases the TS and elastic modulus, but increases the E and WVP. Very strong and stretchable films can be obtained from 70/30 and 60/40 PPC/glycerol compositions, respectively. Film solubility is not affected by the amount of plasticizer (Choi and Han, 2001). Heat treatment of pea-protein isolate solutions for 5 minutes at 90°C to induce denaturation increases the TS and E, and decreases WVP and the elastic modulus. FTIR spectroscopy shows more water in the non-heated than in the heat-denatured ones, while electrophoresis suggests that intermolecular disulfide bonds are created during heat denaturation, which most feasibly results in the observed greater film integrity with respect to the non-heated control films (Choi and Han, 2002).

Table 17.1 References listed by type of protein

Protein	References
<i>Zein</i>	Andres (1984), Ashley (1985), Ben-Yehoshua (1985), Billing (1989), Dombrink-Kurtzman and Bietz (1993), Esen (1987), Foulk and Bunn (1994), Gennadios and Weller (1990), Gennadios <i>et al.</i> (1993a, 1993b), Grenner and Fennema (1989), Krochta (1992), Lai and Padua (1997, 1998), Padua and Wang (2002), Park and Chinnan (1990), Park <i>et al.</i> (1992, 1994a, 1994b, 1994c, 1994d), Parris and Coffin (1997), Rakotonirainy and Padua (1999), Reiners <i>et al.</i> (1973), Santosa and Padua (1999), Seymour and Carraher (1984), Smith (1986), Taylor (1986), Wong <i>et al.</i> (1996), Yamada <i>et al.</i> (1995), Yang <i>et al.</i> (1996)
<i>Soybean</i>	Alcantara <i>et al.</i> (1998), Artnfield <i>et al.</i> (1991), Cheftel <i>et al.</i> (1985), Chen (1995), Feeney <i>et al.</i> (1975), Flint and Johnson (1981), Gennadios and Weller (1993), Gennadios <i>et al.</i> (1993b, 1993c, 1994, 1996, 1998a, 1998b), Ghorpade and Hanna (1996), Ghorpade <i>et al.</i> (1995), Gontard <i>et al.</i> (1993), Kelley and Pressey (1966), Krochta and De Mulder-Johnston (1997), Kunte <i>et al.</i> (1997), Liu (1997), McKay <i>et al.</i> (1985), Naga <i>et al.</i> (1996), Park and Hetiarachchy (2000), S. K. Park <i>et al.</i> (2002), Petersen <i>et al.</i> (1999), Raynes <i>et al.</i> (2000), Rhim <i>et al.</i> (1999, 2000), Shih (1994), Shimada and Cheftel (1988), Sian and Ishak (1990), Stuchell and Krochta (1994), Subirade <i>et al.</i> (1998), Tomihata <i>et al.</i> (1992), Were <i>et al.</i> (1999), Wu and Bates (1972)
<i>Wheat gluten</i>	Ali <i>et al.</i> (1997), Billing (1989), Cuq <i>et al.</i> (2000), Gennadios and Weller (1990), Gennadios <i>et al.</i> (1993b, 1993c, 1993d, 1993e, 1996), Guilbert <i>et al.</i> (2002), Gontard (1991), Gontard <i>et al.</i> (1993, 1995, 1996), Guéguen <i>et al.</i> (1998), Herald <i>et al.</i> (1995), Kasarda (1999), Koelsch (1994), Lafiandra and Kasarda (1985), Micard and Guilbert (2000), Morel <i>et al.</i> (2000), Mujica-Paz and Gontard (1997), Okamoto (1978), Park and Chinnan (1995), Pérez-Pérez (1997), Redl <i>et al.</i> (1999), Watanabe and Okamoto (1976), Wrigley and Bietz (1998)
<i>Cottonseed</i>	Bérot and Guéguen (1985), Besançon <i>et al.</i> (1985), Bizzini and Raynaud (1974), Bourély (1990), Dumay <i>et al.</i> (1986), Gennadios and Weller (1994), Gontard <i>et al.</i> (1993), Guilbert (1986), Guo (1994a, 1994b), Marquié (1987, 1995, 1996), Marquié and Guilbert (2002), Marquié <i>et al.</i> (1995, 1996, 1997a, 1997b, 1998), Means and Feeney (1968), Saroso (1989), Tacher <i>et al.</i> (1990), Tchiegang and Bourély (1990), Wu and Bates (1973), Zongo and Coulibaly (1993)
<i>Other proteins</i>	H. J. Park <i>et al.</i> (2002)
• Peanut	Abogaye and Stanley (1985), Del Rosario <i>et al.</i> (1992), Jangchud and Chinnan (1999a, 1999b), Natarajan (1980), Woodroof (1983), Wu and Bates (1973)
• Rice	Chen and Chang (1984), Gnanasambandam and Hettiarachchy (1995), Gnanasambandam <i>et al.</i> (1997), Houston (1972)
• Pea	Boulter (1983), Choi and Han (2001, 2002), Guéguen <i>et al.</i> (1995, 1998), Jackman and Hada (1989), Linden (1985), Mosse and Pernollet (1983), Nackz <i>et al.</i> (1986), Nickel (1981)
• Pistachio	Ayranci and Çetin (1995), Ayranci and Dalgıç (1992), Crane (1979)
• Grain sorghum	Buffo (1995), Buffo <i>et al.</i> (1997), Dendy (1995), Hamaker <i>et al.</i> (1995), Shull <i>et al.</i> (1991)

Pistachio protein

Pistacia is mainly grown in hot, dry climates, such as in Western Asia, Asia Minor, Southern Europe, Northern Africa, and California. Its fruits (kernels) are used as edible nuts, for making a coffee-like drink, and as a source of oil and coloring (Crane, 1979). Between 35 and 40% of the raw kernel consists of protein, in which the hydrophilic amino acids predominate (e.g. glutamic and aspartic acids) (Ayranci and Dalgıç, 1992). A protein isolate (about 95% protein) can be prepared by extraction from ground kernels, followed by a bleaching process to change the color from brownish to white using hydrogen peroxide, and a coagulation step to obtain the isolate (Ayranci and Dalgıç, 1992; Ayranci and Çetin, 1995).

The protein isolate is combined with hydroxypropyl methylcellulose (HPMC) and PEG as plasticizers to cast films. Film WVP increases with increasing amounts of protein isolate due to the high hydrophilic amino acid content. In addition, films swell by absorbing water, showing a greater thickness with respect to the control HPMC-only film (Ayranci and Çetin, 1995).

Grain sorghum protein

Grain sorghum ranks fifth among cereals produced in the world (Dendy, 1995). The main protein fraction in the sorghum kernel is prolamin, known as kafirin. Kafirin is similar to corn zein in molecular weight, solubility, structure, and amino acid composition (Shull *et al.*, 1991). According to its prolamin nature, kafirin can be readily extracted with alcohol and/or a reducing agent such as β -mercaptoethanol. The addition of β -mercaptoethanol greatly enhances extraction yield, but its toxicity makes it useless if edibility is to be maintained. In sorghum wholegrain flour and sorghum endosperm, the kafirin content is 68–73% and 77–82% of total protein, respectively (Hamaker *et al.*, 1995).

Films have been prepared from laboratory-extracted kafirin (89% protein) (Buffo, 1995) dissolved in ethanol, with glycerin and PEG added as plasticizers. The dry films have similar TS, E and WVP to those of films prepared from commercial corn zein. However, kafirin films are notably darker than zein films, presumably due to a higher content of inherent pigments (Buffo *et al.*, 1997).

Appendix

Table 17.1 lists the references relevant to each type of protein.

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