

CHAPTER II

LITERATURE REVIEW

2.1 Edible film

2.1.1 Definition

Edible films are defined as a thin layer of material which can be consumed, coated on foods or placed as barrier between the food and the surrounding environment (Bourtoom, 2008). Edible films have been developed as food packaging materials because of their abilities to safely protect food products by providing barrier properties, carrying food ingredients, enhancing mechanical integrity of foods while reducing the environmental impact.



(a)



(b)

Figure 2.1 Edible films (a) colorful fruit- and vegetable-based edible films and (b) antimicrobial edible film

Source : USDA (2008)



2.1.2 Film forming materials

2.1.2.1 Polysaccharides-based films and coating

Polysaccharides have been regularly used to make edible film because they are low in cost, plentiful and relatively easy to handle. Examples of commonly used polysaccharide as film forming materials include cellulose derivatives, starch, chitosan, pectin, alginate, glucomannan and carrageenans (Janjarasskul & Krochta, 2010). Polysaccharide films have good mechanical and gas barrier properties but they are generally poor water vapor barriers (Baldwin, Nisperos, & Baker, 1995).

2.1.2.2 Protein-based films and coating

Protein based films can be made from proteins of both animal and plant origins. Common animal proteins used for making protein films are casein, whey protein, meat proteins, egg albumin and feather keratin. For plant proteins, wheat protein, soy protein and corn zein are regularly used for making edible films. Water and ethanol are frequently used solvents in the film preparation process because they are safe for consumption. Most protein films are strong but brittle, therefore, plasticizers are necessary added to casting solution to improve flexibility of films (Dangaran, Tomasula, & Qi, 2009). Generally, protein films have good mechanical and optical properties. In addition, they are good barrier to oxygen, carbon dioxide and aroma. Nevertheless, these films are high in water vapor permeability due to their hydrophilic nature (Janjarasskul & Krochta, 2010).

2.1.2.3 Lipid-based films and coating

Lipids are usually added to edible films to enhance water vapor barrier by increasing hydrophobic component (Baldwin et al., 1997). Edible



lipid films are fragile. Lipid materials can not form cohesive, self-supporting film structure because they do not have repeating units connected by covalent bonds to form a large molecular structure (Janjarasskul & Krochta, 2010). Therefore, they have been incorporated into carbohydrate or protein films to improve moisture barrier properties (Greener & Fennema, 1989).

2.1.3 Plasticizers

Plasticizers are small molecular weight compounds which can be added to film casting solutions to enhance flexibility and elongation, while decrease brittleness of polymeric films. Plasticizers reduce intermolecular forces between the polymer chains, leading to an increase in free volume and improving flexibility (Dangaran et al., 2009). Although incorporation of plasticizer improves mechanical properties, barrier properties of film are typically sacrificed (Krochta & Mchugh, 1994). Common plasticizers used in edible films are polyols (e.g., glycerol, propylene glycol, polypropylene glycol, and sorbitol), sugars (e.g., glucose and honey), and lipids (e.g., monoglycerides, phospholipids, and surfactants) (Dangaran et al., 2009). Plasticizers are normally hygroscopic and attract water molecules. Water can also be used as plasticizers, but it is easily lost due to dehydration in low relative humidity environments (Guilbert & Gontard, 1995). The effectiveness of a plasticizer depends on size, shape and compatibility with the film matrix (Sothornvit & Krochta, 2001).

Laohakunjit and Noomhorm (2004) studied the influence of plasticizer type and concentration on mechanical properties of rice starch film. The tensile strength of rice starch film decreased whereas percent elongation increased with an increased glycerol or sorbitol content. This result might be attributed to the interfering of plasticizer to the arrangement of polymer chains and intermolecular hydrogen bonding. Plasticizer decreased polymer inter-chain interactions, which in turn inducing the flexibility of the films.

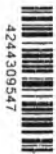


The effect of plasticizer on water vapor permeability of tapioca starch based edible film was studied by Chillo et al. (2008). The researchers found that the glycerol concentration strongly affected the permeability of the starch film. The water vapor permeability increased with incorporating glycerol. It was due to the reduction of polymeric density. This result is in agreement with Laohakunjit and Noomhorm (2004), who found that the oxygen transmission rates of glycerol and sorbitol plasticized rice starch films were significantly increased with increasing glycerol and sorbitol content. These plasticizers were hypothesized to increase mobility of polymer chains.

2.2 Konjac glucomannan

2.2.1 Chemistry

Konjac glucomannan (KGM) is a high molecular weight and water soluble linear polysaccharide extracted from the tuber of *Amorphophallus konjac* plant. KGM is a hydrocolloid and is synonymous with konjac gum and konjac mannan. The main chain comprises of β -1, 4 linked D-mannose and D-glucose with a molar ratio of 1.6:1, with approximately 1 acetyl group at C6 position in every 17-19 sugar units (Liu & Xiao, 2004). The molecular weight of KGM depends on the species of *Amorphophallus* and extraction method (Marceliano, 2009). Li et al. (2006) reported an average KGM's molecular weight of 1.04×10^6 Daltons. If KGM solution is heated after treatment or exposure to alkali, it forms gel. This gelation occurs due to the hydrolysis of acetyl groups which no longer hinder intermolecular hydrogen bonding of chain (Marceliano, 2009).



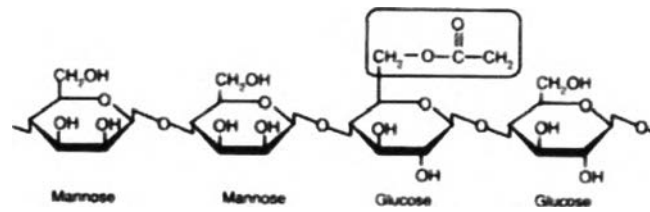


Figure 2.2 Structure of konjac glucomannan

Source : Marceliano (2009)

2.2.2 Konjac glucomannan film formation and properties

Normally, KGM solution is extremely viscous. A 1% KGM aqueous solution gives a viscosity as high as 25000 cP (Marceliano, 2009). KGM film is easy to be peeled from the casting plate. The resulting KGM film is flexible despite the absence of small molecular mass plasticizers. KGM was reported to have enhance water vapor barrier compared to other polysaccharide films (Cheng et al., 2002). KGM film is readily soluble in water which lends itself to application of water dissolve edible film. On the other hand, it is an important obstacle for establishing water resistant packaging. KGM film is translucent and low in gloss, which is typically opposite to preferred visual properties by consumers. Furthermore, one of the major drawbacks of edible polysaccharide films from commercial applications is that they do not possess the ability to be heat sealed.



Figure 2.3 Konjac glucomannan film

KGM films and their applications have been recently explored. Supapvanich, Prathan, and Tepsorn (2012) studied the effect of an edible coating from konjac glucomannan incorporated with pineapple fruit extract on browning inhibition of fresh cut rose apple fruit. The researchers found that the weight loss of fresh cut rose apple fruit coated with konjac glucomannan was lower than that of the control. The incorporation of pineapple extraction in konjac glucomannan film enhanced the browning inhibition of fresh cut rose apple fruit. Wongnimitkul et al. (2009) studied the shelf life extension of fresh cut tomato by using konjac glucomannan film incorporated with antimicrobial agent and clove oil. The researchers found that the konjac glucomannan film with clove oil could extend the shelf life of fresh cut tomato from 11 days to at least 23 days.

2.3 Whey protein

2.3.1 Chemistry

Whey protein is a mixture of globular proteins that remain in milk serum after pH or rennet. The five main proteins include β -lactoglobulins, α -lactalbumins, bovine serum albumin, immunoglobulins and proteose-peptones. The approximate composition and physicochemical characteristics of bovine whey protein is shown in Table 2.1 (Perez-Gago & Krochta, 2002; Walsh, 2002). There are two commercial forms of whey protein available according to their protein content; whey protein concentrate (WPC) contains 25-80% protein and whey protein isolate (WPI) is nearly all protein (>90%). These proteins are heat labile. Denaturation at temperature above 65 °C tend to unfold the globular molecules to a large extent and expose their sulfhydryl groups which are important for food functional properties (Perez-Gago & Krochta, 2002).



2.3.2 Whey protein film formation and properties

Native whey proteins are globular proteins containing hidden hydrophobic and SH groups in the interior of the molecule. On the other hand, heat denatured whey proteins expose internal SH and hydrophobic groups which promote intermolecular disulfide (S-S) bonding and hydrophobic interaction during drying (Shimada & Cheftel, 1998) as shown in Figure 2.4. Both native and heat denatured whey protein films are transparent, glossy, colorless, tasteless, odorless, and having similar water vapor permeability, however, they have different solubility and mechanical properties. Heat denatured whey protein films are insoluble in water and stronger compared to native whey protein films due to the covalent S-S bonding created upon drying (Perez-Gago, Nadaud, & Krochta, 1999). Addition of plasticizer is important to decrease brittleness and increase flexibility of whey protein films. Plasticized whey protein films are transparent, bland, and flexible. Whey protein films have good oxygen, aroma and oil barrier properties, but poor moisture barrier properties due to their hydrophilic group (Perez-Gago & Krochta, 2002).

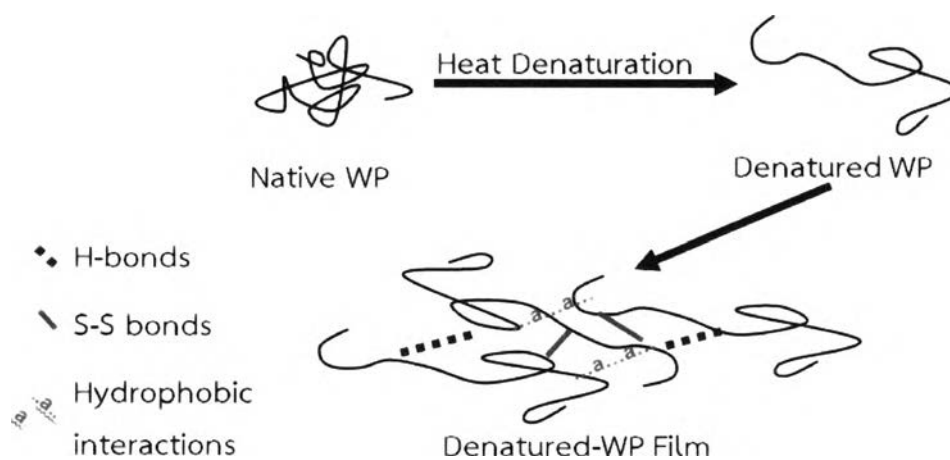


Figure 2.4 Heat denatured whey protein

Source : Krochta and Mchugh (1994)

Table 2.1 Physicochemical characteristics of the major (bovine) whey proteins

	β - lactoglobulin	α - lactalbumin	serum albumin	Immunoglobulin -G	protease- peptones
Approximately composition	57%	19%	7%	13%	4%
Molecular weight (Da)	18,300	14,200	66,300	150,000- 1,000,000	4,100- 22,000
Disulfide bond	2	4	17	nv	0
Sulfhydryl groups	1	0	1	nv	0
No. amino acid residues	162	123	582	1,360	
No. cysteine residues	5	8	35	16	
Isoelectric point (pI)	5.2	4.2-4.8	4.7-4.9	5.5-8.3	

nv = numerous variable

Source : Perez-Gago and Krochta (2002); Walsh (2002)

WPI displays thermoplastic behavior at low moisture level (Hernandez & Krochta, 2008). WPI have been successfully formed into films and sheets using thermoplastic processes such as compression molding and extrusion (Sothornvit, Olsen, & Krochta, 2007) as well as reported to be heat sealable (Kim & Ustunol, 2001).



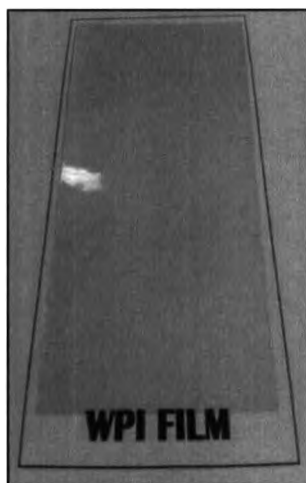


Figure 2.5 Whey protein isolate film

2.4 Composite edible films

Composite edible films are the combination between biopolymers to form films such as proteins and carbohydrates and /or biomaterials such as lipids. The main objective of producing composite films is to take the advantages of each biopolymer composition. Proteins and polysaccharides commonly provide the supporting matrix and enhance barrier to gases. The polar hydrogen-bonding character of polysaccharides and proteins produces films that have high water permeability, low oxygen permeabilities at lower relative humidities and compromised barrier and mechanical properties at higher relative humidities. Lipids are not polymers; therefore, they do not form coherent stand-alone films. However, they can provide gloss and/or moisture-barrier coatings on food surfaces. Moreover, they can constitute the moisture-barrier component of a composite film (Garcia et al., 2009). Therefore, composite films were established for specific applications, aiming to take advantages of complementary functional properties or to overcome flaws of each component (Janjarasskul & Krochta, 2010). Biopolymer composite can modify film properties and create desirable film structure for specific applications. These composite films are applied either in the form of an emulsion, suspension, or dispersion of the non-miscible constituents in a polysaccharide or protein matrix, or



in successive layers (multilayer coating or films), or in the form of a solution in a common solvent (Bourtoom, 2008)

Blending of KGM-based films with other biopolymers such as starch (Chen et al., 2008), gellan gum (Xu et al., 2007), chitosan (Xiao et al., 2000) and gelatin (Li et al., 2006) have been reported. Chen et al. (2008) found that there was a good miscibility between KGM and starch due to hydrogen bonding. The % elongation of starch/KGM blend films was higher than the KGM film. Tensile strength of blend films decreased as starch content increased.

Li et al. (2006) found that the blend system of KGM and gelatin had a good miscibility. The addition of gelatin in KGM film improved heat sealability, water solubility and optical transparency compared to the KGM film. The blend films could be heat sealed at 140 °C and dissolved in the cool water in 30 s. Moreover, tensile strength of blend films was higher than pure KGM or gelatin films because of intermolecular interactions between KGM and gelatin molecules in film matrix.

Xiao et al. (2000) found that there was a smooth surface between chitosan and KGM, however, the miscibility also decreased with an increase of KGM. The mechanical properties of blend films depended on the concentration of KGM. The blend film of chitosan and KGM enhanced the tensile strength due to the hydrogen bonding between chitosan and KGM.

Blending of WPI-based films with polysaccharide such as methylcellulose (MC), hydroxypropylmethylcellulose (HPMC), sodium alginate, and starch have been studied (Yoo & Krochta, 2011). The researchers found that WPI films had the highest transparency. The blend films made of any polysaccharides with WPI had lower transparency than the pure polysaccharides films because of heterogeneous film structures. MC and HPMC blended with WPI gave the highest tensile strength; however, starch-WPI blend films were the weakest films. Water vapor permeability of all films had similar values. In 2012, the same group of researchers studied properties



of corn starch (CS)-MC-WPI blended films (Yoo & Krochta, 2012). They found that CS-MC-WPI blend films were stronger compared to CS-WPI films and had lower oxygen permeability than MC-WPI blend films.

2.5 Drying rate effect

Drying is a process used for removing water or solvent by evaporation from the solid material. Drying rate is defined by the loss of moisture from the wet solid per each unit of time. Overall drying process can be divided into three parts (Chen, 2008):

I. Warm-up period

Material starts to be heated from initial temperature to the wet bulb temperature. The moisture starts to evaporate from the surface. Mass and heat transfer driving forces are non-zero. Concentration of water decreases overtime. Drying process is running on drying curve from point A to point B in drying rate curve, shown in Figure 2.6.

II. First drying period (constant-rate period of drying)

This period begins at point B in Figure 2.6. At this point temperature of the material is equal to the wet thermometer temperature and stays constant. Vapor pressure on the surface of material during constant-rate period is equal to vapor pressure of water on the clean water in the same temperature. In point C moisture content is equal to the critical moisture content. During constant-rate period the drying rate depends on temperature, moisture content and mass flow of air.



III. Second drying period (falling-rate period)

In point C, the surface of the material dries up. The drying rate decreases. Temperature of the material is increasing, and causes decreasing of the mass and heat transfer driving forces. In point E, material temperature is nearly equal to air temperature and moisture content is equal to the equilibrium moisture content. The mass and heat transfer stop at this point and it is not possible under actual conditions to dry material more.

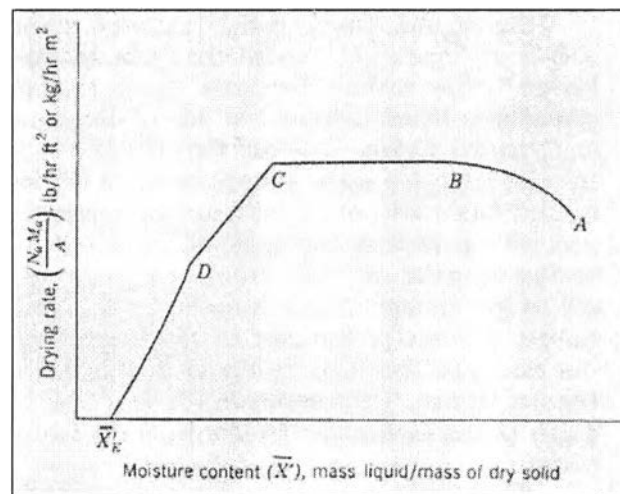


Figure 2.6 Drying rate curve

Source : Chen (2008)

Common practice in edible film formation has been to dry film at ambient temperature and ≤ 50 %RH. However, such drying condition takes long time which is the obstacle for industry scale due to low capability. Therefore, rapidly drying method is required for industrial reasons.

Alcantara, Rumsey, and Krochta (1998) studied the effect of drying rate on the properties of whey protein films. The researchers found that drying rates significantly affected films thickness, WVP and mechanical properties. Rapid drying resulted in less

flexible and stiffer films whereas they had better moisture barrier and thinner in thickness.

Kaya and Kaya (2000) studied the effects of microwave drying on properties of WPI films. The researchers found that the drying time required 5 min in microwave while 18 h at room temperature. The films dried by microwave oven had higher elongation and tensile strength while water vapor permeability was similar compared to the WPI films dried at room temperature.

Mayachiew and Devahastin (2008) found that drying temperature and drying method affected the overall changes of color (ΔE) in chitosan films. Higher drying temperature gave larger changes of ΔE due to higher levels of Maillard browning reactions.

2.6 Storage stability

During storage, the properties of edible films change due to the effect of temperature, %RH and time. The stability of several edible coatings during storage have been investigated by Trezza and Krochta (2000). The researchers studied the color stability of WPI, whey protein concentrate (WPC), zein, HPMC and shellac stored at different temperatures (23, 40 and 55 °C). They found that HPMC coatings had the lowest yellowing rates. WPI coatings had lower yellowing rates than WPC and had similar rate to shellac coatings. Zein coatings became less yellow during storage, however, their color was still pronounced.

Butler et al. (1996) studied the effect of storage time on properties of chitosan films. The researchers reported that oxygen permeability of the chitosan films increased while % elongation decreased over storage time at 23 °C and 50% RH. Those were the sign of film deterioration. Caner, Vergano, and Wiles (1998) also



found that % elongation of the chitosan films decreased with the storage time increased at 22 °C and 40-60% RH.

Heat curing of protein based films during storage has been studied by several research groups. Kim et al. (2002a) reported that heat cured films stored at 60, 72.5 and 85 °C for 24 h were more yellowish than unheated soy protein isolate films. Heat cured film had lower WVP values than that of the control film due to formation of intra- and intermolecular cross-links. Control films had lower elongation and solubility compared to heat cured films. This result is in agreement with Amin and Ustunol (2007). The researchers found that an increasing of heat-cured temperature (80, 90 and 100 °C) and time (12, 24, 48 and 72 h) caused increased tensile strength but decreased solubility due to the additional covalent bonds formed during the heat-curing process.

