DEVELOPMENT AND APPLICATION OF MULTICOMPONENT EDIBLE COATINGS AND FILMS: A REVIEW

YI WU

The Wright Group
Airport Road 6428, P.O. Box 1365
Crowley, LA 70527
USA

CURTIS L. WELLER

Industrial Agricultural Products Center and Department of Biological/
Systems Engineering
and Department of Food Science and Technology
University of Nebraska-Lincoln
Lincoln, NE 68583
USA

FAYRENE HAMOUZ

Department of Nutritional Science and Dietetics
University of Nebraska-Lincoln
Lincoln, NE 68583-0806
USA

SUSAN L. CUPPETT

Department of Food Science and Technology
University of Nebraska-Lincoln, Lincoln
NE 68583-0919
USA

MARILYNN SCHNEPF

Department of Nutritional Science and Dietetics
University of Nebraska-Lincoln
Lincoln, NE 68583-0806
USA

ADVANCES IN FOOD AND NUTRITION RESEARCH VOL 44
ISBN: 0-12-016444-2

I. INTRODUCTION

Deterioration of food texture, flavor, color, aroma or nutritional value is involved in many events associated with undesirable mass transfer. Quality loss of certain foods can occur when they lose or gain moisture, when oxygen diffuses into the foods to cause oxidation or when they experience aroma, flavor or color loss. These mass transfers can happen between foods and their surrounding environment or between components of foods, which result in the reduction of shelf life and food value, and the reduced ability of the food industry to meet increasing consumer demands for higher-quality food products (Krochta, 1992). Edible films and coatings could help prevent such food quality loss. An edible film or edible coating can be defined as a thin layer of material which can be eaten by the consumer, can be applied on or within foods by wrapping, dipping, brushing, or spraying and function as selective barriers against the transmission of gases, vapors and solutes, and also provide mechanical protection (Gennadios and Weller, 1990; Gennadios *et al.*, 1993; Koelsch, 1994; Miller and Krochta, 1997). Besides their barrier properties, edible films and coatings can act as carriers for functional food additives, antioxidants, antimicrobial agents and nutrients (Cuppett, 1994; Cuq *et al.*, 1995). Usually coatings are directly applied and formed on the surface of products, while films are deposed as a continuous layer between food components or formed separately as thin sheets and then applied on the products (Guilbert, 1986; Gennadios and Weller, 1990).

The development of edible films and coatings has received increased interest in recent years due to the increased consumer demand for high quality, long shelf-life and ready-to-eat foods, environmental consciousness for disposal of non-renewable food packaging materials, and the opportunities for creating new market outlets for both traditional and novel agricultural crops which are the sources of the desired film-forming ingredients (McHugh and Krochta, 1994a; Guilbert *et al.*, 1996; Gennadios *et al.*, 1997). Although edible films and coatings offer much potential as mass transfer barriers to improve the quality of foods, industrial applications have been limited. The empirical and uneasy formulation and application procedures of these edible films and coatings make their use and application to foods relatively difficult. Edible film and coating formers are usually categorized into three categories: polysaccharide, lipid, and protein (Kester and Fennema, 1986). Each class of film-former has its distinct functional characteristics. Researchers are now investigating these biopolymers both alone and in combination, as to their effectiveness as edible mass transfer barriers. Progresses, challenges and opportunities in the area of edible films and coatings are presented in recent reviews by Guilbert *et al.* (1996), Gennadios *et al.* (1997), Krochta and De Mulder-Johnston (1997), and Debeaufort *et al.* (1998). However, reviews on the multicomponent edible film systems have been limited.

The aim of this paper is to offer an overview of the research reported in the literature on the combined biopolymer edible films and coatings, which are multicomponent systems, with a focus on their barrier properties. Multicomponent edible films and coatings, terms used interchangeably with composite edible films and coatings, encompass structurally heterogeneous film and coating systems that are composed with more than one edible film-forming material (protein, polysaccharide, lipid) in the form of an emulsion or bilayer. This review will (1) compare the compositions and barrier properties of different multicomponent edible films and coatings; (2) provide insights into the rationale for the effectiveness of these systems; and (3) discuss their potential application on food products.

II. BARRIER PROPERTIES OF EDIBLE FILMS

Barrier properties of edible films include water vapor permeability (WVP), gas permeabilities, volatile permeability and solute permeability. Among gas permeabilities, most edible film researchers are interested in the oxygen (O_2) and carbon dioxide (CO_2) permeabilities because these properties have a bearing on rates of oxidation and respiration in the enclosed foods. Water vapor permeability and O_2 permeability are the most important factors for investigating effectiveness of edible films and coatings. Permeability values can also be used in tailoring film barrier properties for specific food applications and in product shelf-life predictions (McHugh and Krochta, 1994b).

Theoretically, the permeability of a permeant (P), such as water vapor or oxygen, through a polymer film at a given temperature is the product of constant diffusion coefficient (D) and solubility coefficient (S) of the permeant ($P = DS$) when no interaction between the permeant and the film material occur (Pascat, 1986; Krochta, 1992). O_2 permeation occurs primarily by gaseous diffusion whereas water vapor transmission involves both water vapor sorption and diffusion (Banker, 1966). The D and S of the permeant are affected by temperature and by the size, shape and polarity of the diffused molecule. In the case of interactions between the permeant and the polymer film such as water with hydrophilic films, D and S cannot be assumed constant at a given temperature. Therefore, the permeability of a permeant through a film is a function of the following factors: (1) the nature of the film material, (2) the nature of the permeant, and (3) the interactions between the permeant and the films (Pascat, 1986; Shellhammer and Krochta, 1997a). With regard to edible films, which have the tendency to interact strongly with water vapor, the permeability can be thus defined as a property of the film-permeant complex, under specified temperature and water activity conditions (Cuq *et al.*, 1995; Wu *et al.*, 2000). Apparently, different characteristics inherent to the edible film itself play a major role in the process of mass transfer by influencing the diffusivity and solubility of permeants such as water and gas. These characteristics include chemical structure (side chains, chain-to-chain forces), relative polarity, degree of crystallinity, density, molecular orientation, the degree of cross-linking between molecules, molecular weight and polymerization, the presence of plasticizers or additives, etc. (Pascat, 1986; Salame, 1986; Cuq *et al.*, 1995) and are directly associated with the barrier properties of edible films.

Generally, highly polar polymers, such as many polysaccharides and proteins, exhibit extensive hydrogen bonding, resulting in extremely low gas permeability values at low relative humidities (RHs). Unfortunately, the chemical nature that leads to good gas barrier properties often results in poor moisture barrier properties. Highly polar polymers containing hydroxyl groups are often poor moisture barriers. Edible films based on a polar polymer are very sensitive to humidity changes. At low RHs these films tend to crack. At high RHs these films swell and their barrier characteristics are markedly degraded (Guilbert, 1986). Since polysaccharides are monotonous-polymers while proteins have a specific structure that confers more potential functional properties and can be modified easily, polysaccharide base films are more readily disintegrated by absorbing water and have poorer barrier properties than protein base films in general (Cuq *et al.*, 1995). Contrary to polysaccharides and proteins, pure non-polar hydrocarbon-based materials such as lipids exhibit the opposite effects due to their hydrophobic, crystalline nature. These lipid materials have extremely low water vapor permeability, acting as excellent moisture barriers but are less effective gas barriers (Krochta, 1992). However, lipid materials can cause application (adherence and homogeneity), mechanical (break and pinholes) and sensory (waxy and brittle character) problems. They do not form a film and they must be associated with film-forming agents such as polysaccharides (Kester and Fennema, 1989a) and proteins (Torres *et al.*, 1985).

Multicomponent edible films and coatings consisting of blends of various polymers, polysaccharides, proteins and/or lipids have been developed to have cooperative functionalities. In these film systems, the barrier properties may be improved by taking advantage of each constitutive polymer, i.e., a polysaccharide which may impart structural cohesion and serve as a structural matrix; a protein which may give rise to a very tight structure by inter- or intramolecular folding; or a lipid that adds a hydrorepulsive character (Vojdani and Torres, 1990). Most multicomponent films studied to date involve a lipid as a moisture barrier and a high polar polymer as a structural matrix (Guilbert, 1986; Krochta, 1992).

Multicomponent films have been formed by two basic techniques, "coating technique" and "emulsion technique". The former involves casting or laminating a lipid onto a dried edible base film to form a bilayer or laminated film, whereas the latter involves adding a lipid to film-forming solution prior to film casting, and thus creating an emulsified film (Kamper and Fennema, 1984a; McHugh and Krochta, 1994c).

III. POLYSACCHARIDE-LIPID EDIBLE FILMS

Most edible polysaccharide-lipid films for which there are reports in the literature have been cellulose ether-based, mainly methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC)-based films. Other types of polysaccharide-lipid films include pectinate-based and chitosan-based films.

A. WATER BARRIER PROPERTIES

The work by Schultz *et al.* (1949) using low-methoxyl pectinate-lipid films may be one of the earliest studies on the barrier properties of polysaccharide-lipid films. According to their results, pectinate films were better moisture barriers when lipids, including waxes and fatty acids, were incorporated using a coating technique than an emulsion technique. Presumably, the superiority of the surface coatings results from greater continuity of the lipid layer.

The properties of edible films made of various lipid materials either supported by or emulsified with a plasticized HPMC film were first studied by Kamper and Fennema (1984a). For the coated films, lipids were painted onto the surface of the base films while all film components were dissolved in an ethanol-aqueous solution for the emulsified films. Films containing solid lipids such as beeswax (BW), paraffin wax (PW), hydrogenated palm oil (HPO), or stearic acid (SA) yielded much smaller WVP values than films containing liquid lipids such as oleic acid (OA) or vegetable oils and even smaller than that for low density polyethylene (LDPE). Some permeability data of synthetic films can be found in Table I. They suggested that the large difference in permeability between liquid and solid lipids could be explained in terms of the water-vapor solubility in the liquid phase and/or the molecular organization of the lipid. However, films coated with BW, PW and a blend of stearic acid and palmitic acid (SP) were too brittle. Furthermore, the film coated with SP was inferior to the emulsion film with the same fatty acid blend, the HPMC-SP film. A moisture transmission rate of SP coated film was reduced by a factor of about 10 when the fatty acids were incorporated into the film emulsion. This result was counter to that of Schultz *et al.* (1949). The discrepancy between these results may be attributed to the state of the lipid phase in the emulsion (Kester and Fennema, 1986). The ethanol-water solvent system used in Kamper and Fennema's study may make a better emulsion than the aqueous system by the Schultz group.

The HPMC-SP film developed by Kamper and Fennema (1984a) exhibited a very good moisture barrier property at RHs up to about 90% at 25°C (Kamper and Fennema, 1984b). Above 0.90 water activities (a_w), however, the film became hydrated which resulted in a loss in its structural integrity and decreased resistance to water vapor. With an objective to improve the HPMC-SP film, Kester and Fennema (1989a) modified the film by adding MC into the base film to make a plasticized MC-HPMC-SP film and then coated the film with beeswax. This film was very resistant to moisture permeation at a_w up to 1.0 with a 97% RH gradient across the film and had a similar WVP to that of polyvinyl chloride (PVC) and LDPE. The two films were also different in their structures. The surface of the HPMC-SP film was crystalline, consisting of thin platelets characteristic of the SP in solid state while the degree of fatty acid surface crystallinity was much less in the MC-HPMC-SP film. The excellent moisture barrier

TABLE I

PERMEABILITIES OF SYNTHETIC FILMS

Films	Permeability	Thickness (mm)	Temperature (°C)	RH[a] (%)	Reference
Water vapor permeability	($g \cdot mm/m^2 \cdot d \cdot KPa$)				
PVC[b]	0.107	0.025	37.8	0–90	Kamper & Fennema (1984a)
Cellophane	7.27	–	38	0–90	Taylor (1986)
LDPE[c]	0.079	–	38	0–90	Smith (1986)
PVDC[d]	0.012	0.025	37.8	0–90	Kamper & Fennema (1984a)
HDPE[e]	0.02	–	38	0–90	Smith (1986)
Oxygen permeability	($cm^3 \cdot m/m^2 \cdot d \cdot KPa$)				
LDPE	1870	–	23	50	Salame (1986)
HDEP	427	–	23	50	Salame (1986)
Cellophane	252	–	23	95	Taylor (1986)
Polyester	15.6	–	23	50	Hanlon (1992)
EVOH[f] (70% VOH[g])	12	–	23	95	Salame (1986)
PVDC-based films	0.4–5.1	–	23	50	Salame (1986)
EVOH (70% VOH)	0.1	–	23	0	Salame (1986)

[a] Relative humidity difference; [b]polyvinylchloride; [c]low-density polyethylene; [d]polyvinyliodene chloride; [e]low-density polyethylene; [f]ethylene-vinyl alcohol; [g]vinyl alcohol.

property of the MC-HPMC-SP film was attributed to the greater thermal gelation potential and the more hydrophobic nature of the incorporated MC compared to HPMC, which resulted in greater solubility of the cellulose ether in ethanol-water solvent system and the effective entrapment of fatty acids within the cellulose ether matrix.

The MC-HPMC-SP film was also a better base film for supporting a beeswax layer to make a good bilayer film (Kester and Fennema, 1989a). BW was coated onto the base film in a molten state. The fatty acids embedded within the cellulose ether matrix may function to enhance the adhesion of the wax layer to the underlying film, and thus resulting in a bilayer film with the lowest WVP among all aforementioned cellulose ether-lipid films at high a_w up to 1.0.

Taking the advantage of MC, a bilayer film using MC alone as the supporting matrix was developed by Greener and Fennema (1989a). The water barrier property of this molten BW coated MC film (Wax-M) was found to be comparable with the BW coated MC-HPMC-SP film developed by Kester and Fennema (1989a) at a 100% relative humidity (RH) gradient. Beeswax in this study was also dissolved in absolute ethanol at 70–75°C before being coated onto the dried base film to make a bilayer film (Wax-S). Wax-M films had a more uniform surface than Wax-S films as evidenced by scanning electron microscopy (SEM) examination and had an over 60% lower WVP than that for Wax-S films. All these edible bilayer films performed very well at high water activities and large RH gradients in comparison to several non-edible commercial packaging materials.

Martin-Polo *et al.* (1992) developed a MC-based composite film either emulsified with paraffin oil or PW. Neither films showed improved resistance to moisture transmission. When a layer of PW was coated onto the dried MC-PW wax emulsified film, however, the WVP of the so-called emulsion plus coating film was about 30 to 40 times lower than that of the emulsion films. They attributed this difference to the final repartition of the hydrophobic material in the film or over its surface. Emulsified films (even with an ethanol-water solvent system) were observed to have a nonhomogeneous partition of the hydrophobic material due to differences in polarity between the support and the lipids, which resulted in an irregular film surface with spherical masses that were not well incorporated into the base film matrix, whereas the emulsion plus coating film had a continuous coated lipid layer and a uniform surface. Nevertheless, an explanation for the effect of different amounts of PW in the films was not given in the report.

The observation of Martin-Polo *et al.* (1992) was further confirmed in a study by Debeaufort *et al.* (1993). Using the same materials and similar preparation methods but with equal amounts of lipid, a MC-PW emulsified film and a PW coated MC film were developed. The differences of water resistance between the two films essentially depended on the distribution of the hydrophobic materials. The more homogeneously distributed the PW, the more the barrier efficiency increased. Based on SEM observations, they proposed two models to indicate the major influence that structure had on permeability (Figure 1). The "model of series resistance" was for the laminated film and indicates that in laminated films, MC was only used as a support and had no effect on the moisture transfer resistance of the film while the "model of parallel resistance" was for the emulsified film and indicates that water vapor transfer was done preferentially through the hydrophilic matrix in the emulsion film. Therefore, it was possible to estimate with a model the water vapor permeability or resistance of the entire film by starting from the permeability or resistance of each component.

Laminated effective water barriers were also developed by Park *et al.* (1994) by coating a hot solution of corn zein with different types of fatty acid onto a MC base film. Fatty acids used were lauric acid (LA, C_{12}), palmitic acid (PA, C_{16}), and SP (C_{18}-C_{16}). The zein-fatty acid layer was water insoluble and the WVP of the laminated MC-based multicomponent films was reported to decrease as chain length and concentration of fatty acid increased. Fatty acid migration from the corn zein layer to the MC layer was also observed in this study.

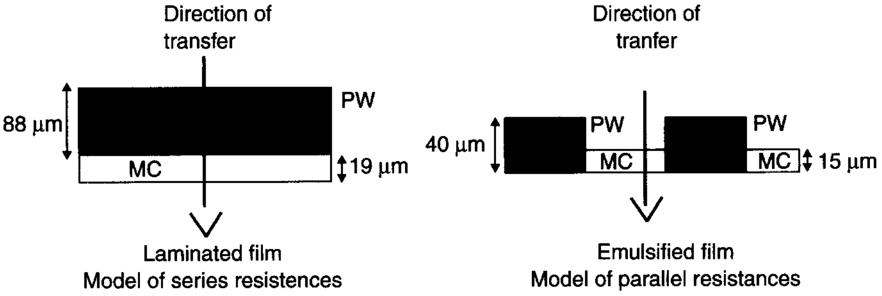

FIG. 1. Schematic representation of the cross-section of films. Water vapor transfer resistance (R) of films can be calculated from the transfer resistance of each layer: methylcellulose (MC) and paraffin wax (PW).

$$R_{laminated} = R_{MC} + R_{PW}$$
$$1/R_{emulsified} = 1/R_{MC} + 1/R_{PW}$$

where R_{MC} is the methylcellulose transfer resistance and R_{PW} the paraffin wax transfer resistance. (Adapted from Debeaufort *et al.*, 1993.)

Lipids, canola oil and lecithin, have been either coated onto or dispersed into a pullulan-rice protein concentrate film matrix (Shih, 1996). The WVPs of the composite films were improved through the addition of canola oil by 32.8% and 51.6% in the emulsified films and the laminated films, respectively. Similarly, 19.0% and 45.1% reduction in WVP values by the addition of lecithin were observed in the emulsified films and the laminated films, respectively.

It is clear that the homogeneous distribution of the hydrophobic material plays a key role either in an emulsified film or a laminated one. However, the main disadvantages of laminated films are that their preparation requires four stages: two coating and two drying stages, which often involve the use of a solvent or high temperatures, and delamination may occur over time (Greener and Fennema, 1989a; Kamper and Fennema, 1984a) due to the high surface energy between polar and nonpolar materials. It is not very realistic for the food industry to adapt to bilayer films. Moreover, use restrictions apply in the case of beeswax, the very low limit set on this wax in food, namely 0.002% (21 CFR, 1988), makes it difficult to use this ingredient in edible films by forming a thin coating. Therefore, homogeneous emulsified films of other lipids with good barrier properties may be more promising for food applications.

After the Kamper and Fennema's emulsified HPMC-fatty acid films (Kamper and Fennema, 1984a), more polysaccharide-fatty acid edible films were also developed using the emulsion technique (Hagenmaier and Shaw, 1990; Koelsch and Labuza, 1992; Sapru and Labuza, 1994, Wong *et al.*, 1992). The effect of fatty acid chain length, concentration and the degree of saturation on WVP of all these emulsified multicomponent films was also studied.

Similar to the finding from the aforementioned laminated MC-corn zein-fatty acid films (Park *et al.,* 1994), resistance to water vapor transmission increased in emulsified HPMC-fatty acid films with an order of SA film > SP film > LA film (Kamper and Fennema, 1984a) and HPMC-fatty acid films with an order of SA > PA > MA (myristic acid, C_{14}) > LA (Hagenmaier and Shaw, 1990). It is believed that fatty acids with shorter chain length have greater chain mobility within the structure of emulsified films and, therefore, allow for greater WVP (Kamper and Fennema, 1984a).

However, Koelsch and Labuza (1992) reported that water vapor permeance decreased as the chain length increased from C_{12} to C_{18} and then increased again as the chain length increased from C_{18} (SA) to C_{22} (arachidic acid, AA). Image analysis revealed that films containing SA exhibited more micro-dispersed fatty acid globules and a greater interlocking network between fatty acid particles than films with the other fatty acids. Based on this interlocking network model (Koelsch and Labuza, 1992; Koelsch, 1994), the increased complexity of the interlocking network results in an increased tortuosity and path distance for a water molecule to travel through the film. The fatty acid chain length may also influence the interlocking capacity within the film. Longer chain lengths may have sufficient steric hindrance to inhibit close packing and the development of an interlocking network while shorter chain lengths may not possess the extensibility essential for the organization of an interlocking network at the concentration (30.3%) used in the study. Scanning electron microscopy (SEM) examination also revealed that the complexity of the structural network in emulsified starch-alginate-fatty acid composite films increased as the chain length of fatty acid increased (Wu *et al.*, 2001a). The incorporation of fatty acids drastically changed the starch-alginate film's structure and the film with 30% SA had a more channeled and tortuous structure than the film with 30% LA or 30% PA (Figure 2). In this study, WVP values of starch-alginate-fatty acid films were generally decreased as chain length of fatty acid increased. Increasing chain length of fatty acids also significantly decreased starch-alginate-fatty acid films' water solubility, another indication of film hydrophilicity and a term developed based on a study conducted by Gontard *et al.* (1994), which will be further discussed later.

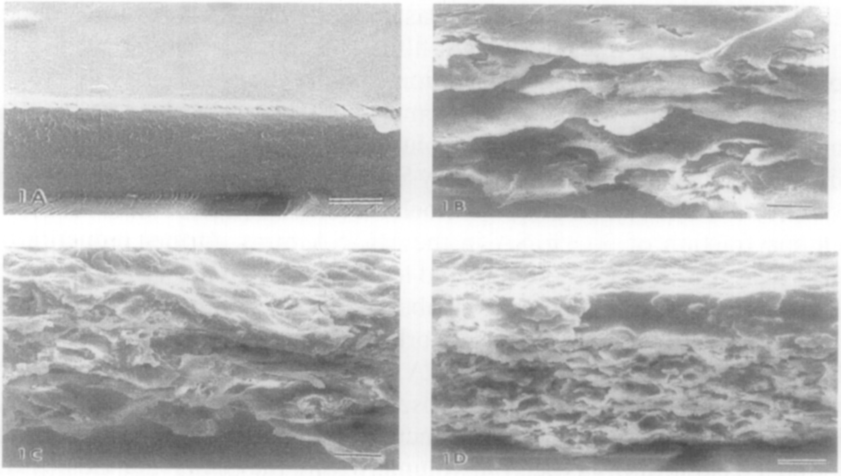

FIG. 2. Scanning electron microscopy photomicrographs of starch-alginate-fatty acid films (fatty acid = 30% starch-alginate, w/w). A: Pure starch-alginate film; B: Starch-alginate-lauric acid film; C: Starch-alginate-palmitic acid film; D: Starch-alginate-stearic acid film. Bar = 20.8 μm.

Surprisingly, in chitosan-lipid emulsified films developed by Wong *et al.* (1992), the result was different. LA was the best one among all other lipid materials tested. The arrangement of stacking layers of chitosan-LA sheets may contribute to the film's low WVP as suggested by SEM examination. A computerized molecular modeling has also been used to explain the results (Pavlath *et al.*, 1993). According to this molecular model, the chitosan-LA system is a helical structure instead of linear (the structure of the chitosan in the absence of LA, which is with the lowest energy level). Most of the LA was shown to be on the inside of the chitosan helical structure by a combination of the acid-base interaction of the carboxyl group of the LA and the amino group of the chitosan, as well as the hydrophobic interactions of the long-chain fatty acids groups. With fatty acid chains shorter than C_{12} the inside diameter is generally large enough for easy migration of the water. The chitosan-LA helix has the smallest diameter. Increasing fatty acid chain length tends to distort the helical structure, with the fatty acid chain moving toward the outside of the helix while the inner diameter of the helix is increasing to allow faster migration of the water.

It has been noted that concentration and unsaturation of fatty acids also affect moisture barrier properties of composite films. Kamper and Fennema (1984b) reported that increasing the stearic acid concentration in the emulsified HPMC-fatty acid films decreased their WVP until a lowest value was reached. Furthermore, the water transmission rate through the HPMC-OA (oleic acid, $C_{18:1}$) film was greater by two orders of magnitude than that through the HPMC-SA film. Hagenmaier and Shaw (1990) found that HPMC-fatty acid emulsion films had decreased WVP as the fatty acid concentration increased from 23% to 45%. However, an increase in permeability occurred above a volume fraction of stearic acid of 46%. Similar results have been reported by Sapru and Labuza (1994) in MC-SA composite films. According to Koelsch and Labuza (1992), above a volume fraction of 30.3% SA in the MC-SA films, further reduction in WVP was less dramatic as compared to the decrease in WVP between 0.0 and 24.4% SA. This may be attributed to the dramatically increased complexity of the interlocking network between the fatty acid particles in the films containing 30.3 to 46.1% SA. Crystal aggregates with significant interspatial air pockets have been observed (Sapru and Labuza, 1994). As the concentration of the fatty acid increased to a certain point, there may be inadequate filling of the void volume within the SA crystallites by the cellulose ether matrix, thus providing open pores with high moisture diffusivity and causing an increase in permeability.

The effect of fatty acid concentration on the WVP and water solubility (WS, another indication of a film's hydrophilicity) of starch-alginate-fatty acid films was also observed by Wu *et al.* (2001a). WS of these composite films exhibited a stronger fatty acid concentration dependency than WVP.

A summary of water vapor permeabilities of some polysaccharide-lipid multicomponent edible films is presented in Table II.

B. FACTORS AFFECTING WATER BARRIER PROPERTIES

1. *Surfactants*

It has been noted that most of the emulsified multicomponent film systems have been developed without the incorporation of an emulsifier or a surfactant because of polysaccharides' ability to act as emulsion "stabilizers". Polysaccharides stabilize an emulsion by steric effect (Callegarin *et al.*, 1997; Figure 3) in that they can protrude significantly into the continuous phase to form a polymeric layer or a network of appreciable thickness. Usually, during drying, "bilayer" films are formed due to the migration of incorporated lipids to the film surface (Kamper and Fennema, 1984a; Kester and Fennema, 1989a; Vojdani and Torres, 1989; Park *et al.*, 1994, 1996a). Debeaufort and Voilley (1995) studied the effect of surfactant on barrier properties of emulsified MC-PW films. Four hydrophobic surfactants (glycerol monostearate – 99% purified GM; acetate GM; 90% purified GM and sorbate monostearate) and two hydrophilic ones (citrate GM and

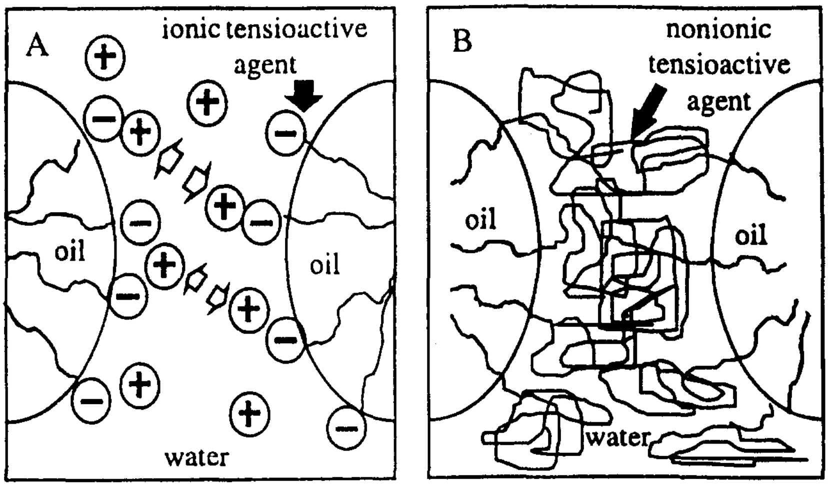

FIG. 3. Representation of interface water-oil: (A) electrostatic repulsion; (B) steric repulsion. (Adapted from Callegarin *et al.*, 1997.)

TABLE II

WATER VAPOR PERMEABILITIES (WVP)[a] OF POLYSACCHARIDE-LIPID MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP ($g \cdot mm/m^2 \cdot d \cdot KPa$)	l (mm)	T (°C)	RH (%)	Reference
HPMC:PEG (9:1)		6.48	0.041	25	0–85	Kamper & Fennema (1984a)
	HPMC:PEG:SP	0.038	0.041	25	0–85	
	SP//HPMC:PEG	1.22	0.041	25	0–85	
	HPMC:PEG:SP	0.34	0.041	25	0–97	Kamper & Fennema (1984b)
	HPMC:PEG:SP	1.92	0.041	25	65–97	
	MC:HPMC:PEG:SP (2.3:1:2:3)	0.26	0.02	25	0–97	Kester & Fennema (1989a)
	MC:HPMC:PEG:SP (2.3:1:2:3)	1.41	0.02	25	65–97	
	BW//MC:HPMC:PEG:SP (BW coating: 4 $mg \cdot cm^{-2}$)	0.057	0.056	25	0–97	
	BW//MC:HPMC:PEG:SP (BW coating: 4 $mg \cdot cm^{-2}$)	0.152	0.056	25	65–97	
MC:PEG (3.3:1)		1.21	0.025	25	0–52	Donhowe & Fennema (1993)
	BW//MC:PEG (3.2 $mg \cdot cm^{-2}$//2.8:1)	0.095	0.05	25	0–100	Greener & Fennema (1989a)
	EC:SP:BW//MC:PEG (0.3:0.2:1//2.8:1)	0.19	0.05	25	0–100	
HPMC		9.12	0.019	27	0–85	Hagenmaier & Shaw (1990)
	HPMC:SA (1:0.8)	0.027	0.019	27	0–85	
MC:PEG (1:0.3)		9.32	0.07	25	23–84	Martin-Polo *et al.* (1992)
	MC:PEG:PO (1:0.3:0.025)	10.38	0.13	25	23–84	
	MC:PEG:PW (1:0.3:0.025)	14.94	0.20	25	23–84	
	PW//MC:PEG:PW	0.35	0.14	25	23–84	
MC:PEG (2.8:0.3)		9.26	0.05	22.6	12–56	Koelsch & Labuza (1992)
	MC:PEG:MA (2.8:0.3:1)	2.95	0.05	22.6	12–56	
	MC:PEG:PA (2.8:0.3:1)	0.56	0.05	22.6	12–56	
	MC:PEG:SA (2.8:0.3:1)	0.19	0.05	22.6	12–56	
	MC:PEG:AA (2.8:0.3:1)	2.89	0.05	22.6	12–56	

TABLE II *(continued)*

WATER VAPOR PERMEABILITIES (WVP)[a] OF POLYSACCHARIDE-LIPID MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP ($g\cdot mm/m^2\cdot d\cdot KPa$)	*l* (mm)	*T* (°C)	RH (%)	Reference
Chitosan		314.64	0.032	25	0–100	Wong *et al.* (1992)
	Chitosan: LA	154.28	0.032	25	0–100	
	Chitosan: PA	233.32	0.032	25	0–100	
	Chitosan: BA	526.68	0.032	25	0–100	
	Chitosan: AM	477.28	0.032	25	0–100	
MC:PEG (3.3:1)		9.32	0.02	25	22–84	Debeaufort *et al.* (1993)
	MC:PEG:PW (3.3:1:3.3)	0.35	0.09	25	22–84	
	PW//MC:PEG (4 $mg\cdot cm^{-2}$//3.3:1)	1.49	0.13	25	22–84	
MC:PEG (10:1)		9.45	0.26	25	0–75	Sapru & Labuza (1994)
	MC:PEG:SA (10:1:1.5)	1.72	0.26	25	0–75	
	MC:PEG:SA (10:1:2.1)	5.94	0.26	25	0–75	
MC:PEG:PW (9:1.9:9)		12.20	0.032	25	22–84	Debeaufort & Voilley (1995)
	MC:PEG:PW:GM (9:1.9:9:0.6)	3.44	0.032	25	22–84	
	MC:PEG:PW:GMC (9:1.9:9:0.6)	7.79	0.032	25	22–84	
MC:PEG (9:1)		24.14^b	–	25	50–100	Park *et al.* (1994)
CZ:PEG:Gly (1:0.22:0.24)		48.44^b	–	25	50–100	
	CZ:PEG:Gly:LA//MC:PEG (1:0.22:0.24:0.4//9:1)	28.36^b	–	25	50–100	
	CZ:PEG:Gly:PA//MC:PEG (1:0.22:0.24:0.4//9:1)	20.00^b	–	25	50–100	
	CZ:PEG:Gly:SP//MC:PEG (1:0.22:0.24:0.4//9:1)	16.90^b	–	25	50–100	

TABLE II *(continued)*

WATER VAPOR PERMEABILITIES (WVP)[a] OF POLYSACCHARIDE-LIPID MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP (g·mm/m²·d·KPa)	l (mm)	T (°C)	RH (%)	Reference
RP:Pullulan:PEG:Gly (10.28:13.72:1:2)		8.78	0.005	21	0–65	Shih (1996)
	RP:Pullulan:Gly:Canola oil (10.28:13.72:1:2:3.2)	5.9	–	21	0–65	
	Canolaoil//RP:Pullulan:PEG:Gly (3.2//10.28:13.72:1:2)	4.24	–	21	0–65	
	RP:Pullulan:PEG:Gly:Lecithin (10.28:13.72:1:2:3.2)	7.11	–	21	0–65	
	Lecithin//RP:Pullulan:PEG:Gly (3.2//10.28:13.72:1:2)	4.82	–	21	0–65	
Starch:Alginate:Gly (5:2:2.1)		5.14[b]	0.106	25	50–100	Wu *et al.* (2001a)
	Starch:Alginate:Gly: Lecithin:LA (5:2:2.1:0.63:2.1)	2.22[b]	0.127	25	50–100	
	Starch:Alginate:Gly: Lecithin:PA (5:2:2.1:0.63:2.1)	2.91[b]	0.103	25	50–100	
	Starch:Alginate:Gly: Lecithin:SA (5:2:2.1:0.63:2.1)	1.25[b]	0.116	25	50–100	

[a] Measured using standard methods; [b]Measured using the WVP Correction Method (McHugh *et al.*, 1993; Gennadios *et al.*, 1994a). "·" = emulsion film; "//" = bilayer film; AA = arachidic acid; AM = acetylated monoglyceride; BA = butyric acid; BW = beeswax; CZ = corn zein; EC = ethylcellulose; Gly = glycerol; GM = glycerol monostearate; GMC = glycerol monostearate citrate, HPMC = hydroxypropyl methylcellulose; l = thickness; LA = lauric acid; MA = myristic acid; MC = methylcellulose; PA = palmitic acid; PEG = polyethylene glycol; PO = paraffin oil; RP = rice protein; PW = paraffin wax; SA = stearic acid; SP = stearic acid and palmitic acid blend; T = temperature during transfer; RH = relative humidity gradient.

Tween 80) were used. Results from their study showed that all hydrophobic surfactants significantly reduced the lipid globule size by 90–95% and WVP by about 40% on average compared to the control MC-PW. Of the six surfactants tested, 0.6% (w/v of emulsion) pure GM produced films that had the lowest WVP, about 70% lower than that of the control. However, these results were dependant on the drying time of the films. They hypothesized that a more homogeneous distribution and smaller-size globules gave better barrier performance, but only when films were dried slowly.

2. *RH*

Although many polysaccharide-lipid composite films have shown improved water barrier properties when compared with their polysaccharide based films, some of these films have been found to have a significantly greater WVP when they are exposed to an environment with high RH. As discussed before, Kamper and Fennema's HPMC-SP film decreased its resistance to water vapor at RH above 90% (Kamper and Fennema, 1984b). This film exhibited greater WVP as the RH gradient was moved upward in the RH spectrum. The WVP value of this film was about 15 times greater for the 97–65% RH gradient than that for the 65–33% RH range. The water barrier developed by Hagenmaier and Shaw (1990) was also found to change its WVP at higher RHs. This HPMC-SA (40–50%) film maintained its high water resistance when RH was raised from 85% to 94%. At 97% RH, however, the WVP was about four times its value at 94% RH, and at 99% RH it again doubled. Koelsch and Labuza (1992) also demonstrated that the WVP values of various MC-fatty acid films was a function of the a_w gradients. Interestingly, their results showed that films with highest WVP values at an a_w gradient of 0.56–0.12 exhibited the largest increase in permeability at a smaller a_w gradient of 0.56–0.44 but higher average a_w. However, the WVP of the MC-SA (30%) films, the best barrier found in their study, was not affected by the change of a_w gradient.

Donhowe and Fennema (1992) tested the water vapor permeance of a series of bilayer films, i.e. BW and BW-acetylated monoglycerides (BW-AM) coated MC films, BW and BW-AM coated carboxymethylcellulose films, and BW and BW-AM coated ethylcellulose (EC) films at RH gradients of 100–0%, 100–50%, 100–65% and 100–80%. All films, except those containing EC, exhibited increased moisture content and WV permeance as the RH gradient was reduced by raising the low-end RH. Because of its hydrophobicity, EC films behaved differently.

The hydration and swelling of the hydrophilic structure matrix in these films may facilitate water movement through the film, the plasticization of water absorbed in these films may increase the mobility of water molecules, thus causing the decreased water resistance of these films at high RHs (Rouse, 1947). Investigating the WVP of edible films at relatively small gradients in the upper half of the RH spectrum is useful because these conditions are far more common to foods than are the 100–0% gradients that are often used when evaluating films.

3. *Temperature*

Temperature is another important environmental factor that may influence WVP of edible lipid composite films. Kamper and Fennema (1984b) observed approximately a six-fold elevation in WVP through their HPMC-SP emulsified film upon reduction of the temperature from 25°C to 5°C. However, a similar film exhibited substantially better properties at –20°C than it did at 5°C (Kamper and Fennema, 1985). According to Kester and Fennema (1989a), the WVP for the BW coated MC-HPMC-SP laminated film at 4°C was still slightly less than at 25°C though a slight increase in WVP at 4°C was also noted, which was attributed to minor defects or flaws in the film caused by the lipid contraction. Furthermore, BW coated MC-HPMC-SP laminated film had a good stability against fracture at the low temperature. There was only a small increase in the average WVP after three and nine weeks of storage at –40°C.

Similar results were obtained by Greener and Fennema (1989a) with the BW coated MC films. The WVP of these film did not change significantly after being stored at –40°C for one week. Structural examination showed that low temperature did not cause any visible cracks or breaks to develop in the film and these films also did not exhibit any tendency to delaminate. These results suggested that these films would function well in frozen food due to their tolerance to low temperature.

Results from a model system have shown that as temperature increased, the resistance of lipids to the transmission of water vapor increased and this temperature dependence of resistance to water vapor transmission was influenced markedly by the polar-supporting matrix. This was attributed to the moisture sorption characteristics of the support matrix (Kester and Fennema, 1989b). This finding may be applicable to edible lipid composite films.

C. OXYGEN BARRIER PROPERTIES

Pure polysaccharide films usually have good gas barrier properties at low RHs. However, their gas permeabilities increase when the content of added plasticizers increases. The addition of lipids can also improve the gas barrier properties for these films. Park and Chinnan (1990) measured the gas permeabilities of a bilayer film at 30°C and 0% RH. They found that increasing the plasticizer content by 10% in HPMC and MC films increased O_2 and CO_2 permeabilities. The addition of a lipid, acetylated monoglycerides (AM), to the film-forming solution significantly decreased its O_2 and CO_2 permeabilities by approximately 65% and 90%, respectively.

Coating BW onto the plasticized MC base layer resulted in an oxygen resistance that was comparable to many commercial packaging materials as reported by Greener and Fennema (1989a). They also found the BW coated plasticized MC-SP film, which contained fatty acids in the hydrocolloid base layer, retained good barrier properties when exposed to a 97–65% RH gradient and proposed that inclusion of lipids in the base layer appeared to lessen hydration of this layer and thereby help the lipid coating retain its barrier properties.

Park *et al.* (1996a) developed a laminated film by coating corn zein-fatty acid solution onto a plasticized MC layer, which was similar to the one developed by the same research group in 1994. Fatty acids used were LA, PA and SP. They observed fatty acid migration from the corn zein layer to the MC layer after these films were stored for 5 days at 50% RH, and the fatty acids distribution increased with concentration and chain length of fatty acids. O_2 permeability, of both the laminated films and the MC layer separated from the laminate, increased as chain length of fatty acids decreased and concentration of fatty acid increased.

O_2 permeabilities of some multicomponent edible films are summarized in Table III.

D. FACTORS AFFECTING OXYGEN BARRIER PROPERTIES

1. RH

The effect of RH on the O_2 transmission rate of a plasticized MC-PA emulsified film has been studied by Rico-Pena and Torres (1990a). RH affected the hydration status of the film and thus its permeability. No significant increase in O_2 transmission rates was observed between 0–57% RH. However, above 57% RH an exponential increase in O_2 transmission rates resulted and the film permeability was doubled at 79% RH. They also found that O_2 transmission rates as a function of RH agreed well with the moisture uptake of the film as affected by RH conditions.

2. Temperature

O_2 permeability could also be temperature dependent although no data are available at this moment. Kester and Fennema (1989c) have reported that the majority of lipid films displayed decreased O_2 resistance when

TABLE III

OXYGEN PERMEABILITIES OF MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	Permeability ($cm^3 \cdot m/m^2 \cdot d \cdot KPa$)	l (mm)	T (°C)	RH (%)	Reference
Polysaccharide-lipid films						
Chitosan		3.49	0.032	25	0	Wong *et al.* (1992)
	Chitosan: LA	7.93	0.032	25	0	
	Chitosan: PA	0.44	0.032	25	0	
	Chitosan: BA	–	0.032	25	0	
	Chitosan: AM	0.15	0.032	25	0	
Protein-lipid films						
WG:Gly (2.5:1)		3.88	0.127	23	0	Gennadios *et al.* (1993b)
	WG:Gly:MO (2.5:1:0.33)	3.30	0.125		0	
WG:Gly (2.5:1)		3.88	0.101	23	0	Gennadios *et al.* (1993c)
	WG:Gly:AM (2.5:1:0.33)	2.72	0.066	23	0	
WPI:Sor (1:1)		8.3	0.11	23	50	McHugh and Krochta (1994e)
	WPI:Sor:BW (3.5:1.8:1)	11.6	0.11	23	50	
WG:Gly (5:1)		2.41	0.14	25	0	Gontard *et al.* (1996)
WG:Gly (5:1)		23.28	0.14	25	56	
	BW//WG:Gly:BW (5:1:1.5)	19.4	0.14	25	56	
	BW//WG:Gly:DTEM (5:1:1.5)	21.34	0.14	25	56	
WG:Gly (5:1)		1905	0.14	25	91	
	WG:Gly:BW (5:1:1.5)	1332.78	0.14	25	91	
WG:Gly (5:1)		2502.6	0.14	25	95	
	WG:Gly:DTEM (5:1:1.5)	1532.6	0.14	25	95	

TABLE III *(continued)*

OXYGEN PERMEABILITIES OF MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	Permeability ($cm^3 \cdot \mu/m^2 \cdot d \cdot KPa$)	l (mm)	T (°C)	RH (%)	Reference
Other type of multicomponent films						
WG:Gly (2.5:1)		3.88	0.127	23	0	Gennadios *et al.* (1993b)
	WG:Gly:Keratin (2.5:1:0.33)	0.58	0.119	23	0	
WG:Gly (2.5:1)		3.88	0.101	23	0	Gennadios *et al.* (1993c)
	WG:Gly:SPI (2.5:1:0.75)	2.33	0.08	23	0	
	WG:Gly:Zein (2.5:1:0.75)	4.07	0.072	23	0	

"·" = emulsion film; "//" = coated or laminated onto = biayer film; AM = acetylated monoglyceride; BA = butyric acid; BW = beeswax; DTEM = diacetyl tartaric ester of monoglyceride; Gly = glycerol/glycerin; l = thickness; LA = lauric acid; MA = myristic acid; MO = minera oil; PA = palmitic acid; SA = stearic acid; SPI = soy protein isolate; T = temperature during transfer; WG = wheat gluten; RH = relative humidity.

temperature was increased. This implies that temperature might affect the O_2 permeability of bilayer films when lipids are added.

E. SOLUTE BARRIER PROPERTIES

Compared to research on WVP and O_2 permeability, few studies have been directed to the control of the diffusion of other molecules, particularly food preservatives. Information in this area found in the literature is mainly based on studies conducted in the Department of Food Science and Technology at Oregon State University. These studies (Torres, 1987; Vojdani and Torres, 1989, 1990; Rico-Pena and Torres, 1991) have been focused on the use of edible films to control the diffusion rate of an antimicrobial agent, potassium sorbate that is applied on the food surfaces, into the food and eventually solve surface microbial stability problems. Most of the edible films that have been tested for this property were polysaccharide films while a few of them were multicomponent systems.

Several cellulose ether-lipid composite films have been developed in the late 1980s by Vojdani and Torres (1989, 1990). These films included: (1) MC or HPMC-fatty acids emulsified films (Vojdani and Torres, 1990). Fatty acids used were LA, PA, SA, AA, elaidic acid (EA, $C_{18:1}$, *trans*), OA; (2) bilayer films (Vojdani and Torres, 1989) – a MC-fatty acid (45:20) emulsion was cast onto a dried MC base film or a HPMC-fatty acid (45:20) emulsion was cast onto a dried HPMC base film. Fatty acids used were LA, PA, SA or AA; (3) coated films (Vojdani and Torres, 1989) – MC or HPMC base films were coated with a hot solution of lipids which were HPO, BW, or SP (50% w/w); (4) multiple layer films (Vojdani and Torres, 1989) – a SP mixture (50% w/w) was embedded between two layers of HPMC. Generally, all these composite films significantly lowered the potassium sorbate permeability (PSP) relative to cellulose ether films containing no lipids.

The PSP in the first group of films decreased as chain length and concentration of fatty acid increased (Vojdani and Torres, 1990). At all fatty acid concentrations the lowest permeability values were obtained for AA. However, film casting difficulties interrupted the tendency towards lower permeability values as the fatty acid concentration increased to cellulose ether–fatty acid ratio of 45:20, particularly with SA and AA. Unsaturation of fatty acid also affected the PSP of the lipid films. At MC:fatty acid ratio of 45:15, PSP value of MC-EA and MC-OA films was close to those of LA films but 1.7 and 2.1 times higher than that of SA, receptively.

Different from the above results, the lowest PSP value was observed for MC-PA films among the bilayer films (Vojdani and Torres, 1989). Furthermore, at higher fatty acid concentration film casting difficulties were not noticed and the PSP values of the bilayer films were lower than those for emulsified films in general, indicating an improvement for films cast on top of a base film relative to those cast on glass. Therefore, food surface properties may affect the coating properties. In the case of coated films, HPO and SP coated HPMC films formed poor films due to their brittleness; whereas BW coated HPMC films exhibited extremely low PSP values compared to all Vojdani and Torres' films and were very flexible. This was attributed to a uniform coverage of the wax on the film's surface, which was evidenced by the scanning electron microscopy studies.

F. FACTORS AFFECTING SOLUTE BARRIER PROPERTIES

1. RH

Similar to WVP and O_2 permeability, the PSP of cellulose ether-fatty acid emulsified films can be affected by environmental RH or water activity. Rico-Pena and Torres (1991) noted that the PSP of MC-PA emulsified films increased as a_w increased and the stability of these films was affected when exposed to environments with a_w above 0.80 due to the hydration of the films.

2. Temperature

The effect of temperature on the PSP of cellulose ether-fatty acid emulsified films was also studied by Vojdani and Torres (1990). Permeability determinations of MC or HPMC-fatty acid films at 5, 24, 32 and 40°C showed excellent agreement with the Arrhenius activation energy model for the permeation process. This suggested that it should be relatively simple to interpret storage stability studies under changing storage temperatures for foods with such films. They also reported that an equation derived from the Stokes-Einstein equation: $K^*\mu/T = \alpha$ (K = permeability value; μ = solvent viscosity; T = absolute temperature; α = a constant) for the diffusion of a molecule in a medium of known viscosity may be used to estimate the permeability of the cellulose ether-fatty acid films and the effect of cellulose ether-fatty acid films on increased surface microbial stability may also be predicted (Vojdani and Torres, 1990; Torres, 1987).

G. APPLICATION OF POLYSACCHARIDE-LIPID FILMS

Several differentially permeable, multicomponent edible coatings for fruits and vegetables were developed and introduced in the market in the mid-1980s. These coatings are mixtures of sucrose esters of fatty acids, mono- and di-glycerides, and the sodium salt of carboxymethyl cellulose. Such coating formulations are commercially available with the trade names TAL Pro-long (later Pro-long, Courtaulds Group, London) and Semperfresh (United Agriproducts, Greeley, Colorado; Inoteh International Co. Mentor, OH) (Baldwin, 1994; Avena-Bustillos and Krochta, 1994). The latter claims to be an improved formulation that consists of a high proportion of short chain fatty acid esters (Drake *et al.*, 1987). These coatings have been applied successfully to retard ripening on bananas (Banks, 1984), apples (Smith and Stow, 1984; Drake *et al.*, 1987), pears (Meheriuk and Lau, 1988), and mangoes (Dhalla and Hanson, 1988). The most marked effect of this coating has been reported to be an increased internal CO_2 concentration (Smith and Stow, 1984). TAL Pro-long has been reported to effectively retain or increase the volatile compounds important to fresh orange flavor in pineapple orange juice (Nisperos-Carriedo *et al.*, 1990).

Polysaccharide-lipid edible films have been applied on several food systems or bicomponent model food systems. However, these application studies have focused only on the moisture barrier properties. The HPMC-SP emulsified film developed by Kamper and Fennema (1984a) was situated between two food components of markedly different water activities by Kamper and Fennema (1985) to determine the film's ability to retard equalization of water activity. Tomato paste or salted tomato paste was used as the high-moisture food and ground crackers were used as the low-moisture food. The composite film was found to substantially slow water transfer from the tomato paste to the crackers during 14 days at 25°C and 21 days at 5°C. During 70 days at –20°C, the film essentially stopped the transfer of water from tomato paste to the crackers.

Using another bicomponent model food system consisting of bread and a tomato-based sauce, Kester and Fennema (1989d) placed the BW coated MC-HPMC-SP laminated at the interface of the two components. The film effectively retarded migration of moisture from the sauce to the bread during frozen storage (–6.7°C for 9 weeks) and the desirable sensory properties were maintained significantly better in the presence of the film than they were in its absence.

BW coated MC laminated film has also been applied on the surface of brownies (Greener and Fennema, 1989b) as a moisture barrier. When brownies were stored at 100% RH and 25°C, the film significantly decreased moisture absorption as compared to that of control samples.

Rico-Pena and Torres (1990b) tested a plasticized MC-PA emulsified film and a pure MC film as moisture-impermeable barriers in a simulated sundae ice cream cone. Circular pieces of film were arranged between the sugar cone and the chocolate layer of samples. Sugar cones of samples containing MC-PA films showed no detectable moisture increase for 10 weeks at –23°C and for 4 weeks at –12°C and only negligible increments after that. Moisture increase was greater in samples with pure MC films. Both films retained the crispness of the sugar cones longer than three months, which is the commercial storage-life of the uncoated product.

The corn zein-SP coated MC laminated films developed by Park *et al.* (1994, 1996a) have been tested as packaging for potato chips (Park *et al.*, 1996b). The laminated films were heat-sealable and could be formed into packaging bags. A shelf-life test showed that the maximum storage times for acceptable potato chip quality were: 30 to 43 days, 23 to 25 days, and 11 to 12 days for storage temperatures of 15, 25 and 35°C, respectively. Chip quality was not affected by the various concentration of SP in the corn zein layer used in the study.

Moisture loss of precooked ground beef patties packaged in heat-sealable starch-alginate-stearic acid films was also tested in a recent study (Wu *et al.*, 2001b). Comparing to samples packaged in the control starch-alginate films, moisture loss was significantly lessened in samples packaged in the composite films over the 6-day storage period at 4°C. However, these composite films were inferior to polyester bags in controlling moisture loss and they slightly swelled over time.

IV. PROTEIN-LIPID EDIBLE FILMS

A number of plant and animal proteins have been used for producing edible films and coatings. These proteins include corn zein, wheat gluten, soy protein, peanut protein, keratin, collagen, gelatin, and milk proteins including casein and whey proteins (Gennadios *et al.*, 1994b).

Possibilities of improving barrier properties of protein films through the addition of hydrophobic lipid materials have been explored but less extensively than polysaccharides for use in multicomponent film systems as a structural matrix. Ukai *et al.* (1976) has identified the potential of protein-lipid emulsion coatings as effective mass transfer barriers in a patent but most of the earlier experiences with protein-based films appear to involve their formation properties. Until recently, more permeability data are available for protein-lipid films.

Most of the protein-lipid films developed to date have been emulsified multicomponent systems due to the easier preparation procedures relative to laminated films. Protein-lipid emulsion films can be formed from aqueous solutions and applied to foods at room temperature. Also, by taking advantage of the good emulsification properties of proteins (Leman and

Kinsella, 1989), film systems can be formed with a more homogeneous distribution of the lipid particles. Protein stabilizes an emulsion by "electrostatic effect" between the lipid polar head and protein polar groups (Figure 3) and "hydrophobic forces" between the lipid hydrocarbon chain and protein hydrophobic groups (Callegarin *et al.*, 1997). Usually, a plasticizer is also added into the films to increase the film flexibility.

A. WATER BARRIER PROPERTIES

1. Gelatin and casein-based films

Guilbert (1986) investigated the effectiveness of emulsified films consisting of a blend of stearic acid-palmitic acid and carnauba wax (ethanolic solution) in a gelatin or casein aqueous structural matrix. These films formed bilayers during drying. No permeability data was reported but the resulting films were described as good water barriers, being brittle and not transparent with a waxy taste.

Krochta and coworkers (1990) took the advantage of the emulsifying capabilities of casein to create casein-lipid emulsion films with improved moisture barrier properties. These casein-based films, lipid materials such as AM, BW, carnauba wax and PW provided resistance to moisture movement, while the casein provided structural cohesion, bound the film to wet surfaces, and reduced the waxy appearance. Their results showed that casein-AM emulsified films reduced the moisture loss by one-half compared to casein/glycerin films at room temperature and 0–100% RH. Double the amount of AM relative to casein reduced moisture permeability by another 50%.

Avena-Bustillos *et al.* (1990) further studied films made from aqueous emulsions of caseinate with AM. Stable emulsions were formed which provided entrapment of lipid droplets as the water-solvent evaporated. Permeability measurements indicated that AM did separate from the emulsion and migrated to the surface to some degree. The result was a lower WVP when the upper (air) side of the cast film faced the high RH in a permeability test cell. Avena-Bustillos *et al.* also found that calcium caseinate-AM film had a WVP that was approximately 30% less than that of sodium caseinate-AM film.

It was found that WVPs of pure caseinate films could be reduced by over 70% through incorporation of lipid materials (Avena-Bustillos and Krochta, 1993). Casein could form aqueous emulsions with AM and moderate levels of SA and BW. WVPs of these films decreased as lipid concentration increased. Addition of BW produced orientation effects, and differences in WVPs due to film orientation increased as the amount of the lipid increased. Among all lipids tested, BW films were the most effective films to reduce WVP. These casein-based films were found to be nearly invisible, adhere well to wet surfaces, and have a bland flavor that will not interfere with the sensory attributes of uncoated products.

2. *Wheat gluten-based films*

Wheat gluten-lipid films have been developed by two groups of researchers. Gennadios *et al.* modified wheat gluten films by the incorporation of mineral oil (Gennadios *et al.*, 1993b) and two types of AMs (Gennadios *et al.*, 1993c). Films containing mineral oil lowered the WVP of the control wheat gluten film by 25% while films with AMs did not change the water barrier property over the control film.

Studies conducted by Gontard *et al.* (1994, 1995) revealed that the effect of lipids on the functional properties of wheat gluten-based composite films depended on the lipid characteristics, the interaction between the lipid and the protein structural matrix and the film preparation methods. Hydrophobicity of the lipids affected the WVP of the gluten composite films. Among 11 lipids used in wheat gluten-lipid emulsified films developed in one of the studies (Gontard *et al.*, 1994), BW was found to be the most effective one for improving the WVP of films as in aforementioned polysaccharide-lipid films, but these films were opaque, weak and disintegrated easily in water. Due to its high melting point, carnauba wax solidified quickly, formed distinct particles during drying, which made it difficult to mix in protein solutions and resulting in the limited barrier properties and the unacceptable optical properties of the carnauba wax composite films. In contrast to these high melting-point waxes, hydrophilic lipid components such as soy lecithin and AM increased the WVP of the films. The presence of hydrophilic groups in these lipids promoted water molecule sorption, thus providing easier water vapor migration through the film. Most of these materials had substantially high steric dimensions, which may have affected their ability to associate with protein chains. In this case, the protein structural matrix could stretch and with a resulting overall loss of water barrier properties of the film. However, diacetyl tartaric ester of monoglycerides (DTEM) markedly improved the water resistance of the films even though it had a relatively large hydrophilic group. This may be attributed to its strong effect on gluten, especially in strengthening the protein structural matrix (Gontard *et al.*, 1992). Combining wheat gluten with this lipid material also increased film strength and maintained transparency. Stearic alcohol and OA also decreased WVP of the films, but the former was more effective due to its less hydrophilic polar hydroxyl groups than the carboxyl group of OA. Also, as discussed in the polysaccharide-lipid film section, unsaturated fatty acids possess a certain degree of mobility due to their double bonds, which can reduce the density of lipid molecules in an emulsified film structure and thus its moisture barrier properties (Kamper and Fennema, 1984a).

It is noted that "dispersion in water" or "water solubility (WS)" was first determined by Gontard *et al.* (1994) in the above study using 11 lipids. Film dispersion in water was found to increase sharply beyond a certain lipid concentration. Above this threshold, the presence of a lipid component may reduce the intermolecular interactions between protein chains or decrease water resistance when the lipid component is hydrophilic. Therefore, "dispersion in water" or "WS", similar to WVP, is another indication of a film's hydrophilicity and it is related to the film's integrity.

In another study conducted by Gontard *et al.* (1995), laminated wheat gluten-lipid films were developed. Films were prepared by depositing a thin layer of lipid onto the surface of a dried wheat gluten base film and a dried wheat gluten-DTEM emulsified film that was similar to that developed earlier by the same researchers (Gontard *et al.*, 1994). All lipids were coated on the base films using the molten method except for BW, which was also applied, with a solvent method. Results obtained from the study showed that WVP of two types of base films were improved by coating the lipid layer. Solid lipids such as BW or PW deposited in a molten state onto the base film produced the most effective water vapor barriers. BW coated films with wheat gluten-DTEM base films exhibited significantly lower WVP than those with the wheat gluten only base film. BW adherence to the base film might be improved due to the presence of a lipid component (DTEM) in the base film. Using an emulsified composite film as a base in the fabrication of bilayer films could improve the adhesion of the coated lipid layer. In this study, the BW coated wheat gluten-DTEM film had an extremely low WVP of 0.036 g•mm/m^2•d•KPa, which was less than that of LDPE.

3. Soy protein-based films

Edible films from soymilk are known as "yuba" in Japan and "to-fu-pi" in China. Interestingly, these oriental traditional products are natural multi-component edible films which consist of soy protein (about 50%) and lipids (about 28%) as the main constituents with the rest being carbohydrates and ash (Wu and Bates, 1972). The creamy yellow films, when still wet, are used for wrapping meats and vegetables. Upon drying, they become brittle and are shaped into sheets, sticks, and small flakes for further use in wrapping and cooking (Snyder and Kwon, 1987). However, no data is available on the barrier properties of these soy protein-lipid films.

Information on water barrier properties of other types of soy protein-based edible composite films are also limited. Recently, soy protein isolate (SPI)-fatty acid edible composite films has been developed using the emulsion technique (Rhim *et al.*, 1999a). WVP of SPI was significantly decreased by the incorporation of LA, PA, SA and OA with a reduction of 260% for films with 40% PA and SA. However, adding fatty acids had little effect on WS of the composite films except for the LA film, in which LA adversely affected the WS and the effect became more severe as the concentration of the fatty acid increased. WVP and WS of biodegradable soy protein-fatty acid films have also been reported to be less than the protein films without fatty acid (Gennadios *et al.*, 1997b).

4. Corn zein-based films

Currently, no WVP data of corn zein-lipid multicomponent films are available from the published literature. However, water barrier properties of corn zein-lipid sheets have been studied through examining their water absorption behavior by Lai *et al.* (1997). Corn zein is unique in terms of thermoplasticity and hydrophobicity. The thermoplasticity of corn zein makes it possible to form a sheet type of film. The hydrophobic nature of corn zein is attributed to its high content of nonpolar amino acids (Gennadios *et al.*, 1994). Thus one may expect corn zein films would possess high moisture resistance. However, films prepared from corn zein are known to be very tough and brittle (Gennadios and Weller, 1990) and require the addition of plasticizer to improve the flexibility and reduce the risk of chipping, cracking, and shattering (Andres, 1984; Torres, 1987). Decreases in the tensile strength of plasticized corn zein film as RH increased have been observed, and substantial increases in equilibrium moisture content with increases in RH have been documented for corn zein films (Gennadios *et al.*, 1993a). Therefore, it is necessary to improve the water resistance of plasticized corn zein films. In the study conducted by Lai *et al.* (1997), fatty acids, PA and SA, were incorporated into corn zein to fabricate zein-fatty acid plasticized sheets while flax oil was coated (once or twice) onto corn zein sheets with no fatty acid added to form oil coated zein sheets. It was observed that fatty acid-zein sheets become soft but retain their shape while the control corn zein sheet disintegrated easily after two hours of soaking in water. The addition of fatty acids reduced water uptake of zein sheets. Water absorption also decreased continuously with increasing fatty acid content. Kinetic parameters suggested that fatty acids decreased water absorption by decreasing the water saturation level of zein sheets. PA was more effective than SA in controlling water absorption. The structure of the control zein sheet was amorphous and showed cracks and voids under SEM while the layer structure of zein-fatty acid films apparently sandwiched the protein between lipid layers and reduced the exposure of protein to water. PA had a better distribution throughout the zein resin. Coating corn zein sheets with flax oil changed the water absorption behavior from capillary movement (in the control sheet) to diffusion (oil coated sheet) by sealing off surface pores, thus decreasing the rate of water absorption. Two layers of oil coating were more effective than one layer of coating.

5. *Whey protein-based films*

Research on exploring the potential for whey protein acting as a structural matrix for edible films began only recently but has drawn more and more research attention. The relationship between WVP and protein-lipid interaction in whey protein-lipid emulsified films has been the focus in some of the most recent studies. Whey protein isolate (WPI) has been the structural matrix in these whey protein-lipid film studies.

McHugh and Krochta (1994c) investigated the effect of incorporating various lipids into WPI-based edible films. AM, waxes, fatty alcohols, and fatty acids were used. The addition of lipids to WPI film systems significantly lowered film WVP in any RH environment. The effect of lipid type on WVP was also significant and this was correlated with their melting points. BW emulsified films had the lowest WVP followed by PA films and then fatty alcohol ones. Therefore, lipid melting points may be used as a gross indicator of film WVP. Increasing fatty acid and fatty alcohol chain lengths and concentration reduced WVP of WPI-lipid emulsified films. It was noted in this study, however, film orientation had a significant effect on WVP due to the formation of partial bilayer films during drying. Also, films could not be cast from LA or SA emulsion due to their extremely high, gel-like viscosity. The protein-lipid film structure was first examined using SEM in this study. The micrographs revealed the presence of crystalline lipid particles within the protein matrix of the emulsified films. Transmission electron microscopy (TEM) examination of WPI-lipid films confirmed the presence of discrete crystalline lipid particles in the emulsified films.

Similar to the findings of Debeaufort and Voilley (1995) in MC-PW emulsified films, the moisture barrier properties of WPI-BW were also significantly affected by lipid particle size and distribution (McHugh and

Krochta, 1994d). Linear decreases in average film WVP values were correlated well with decreasing mean emulsion particle diameters. Unlike the tortuosity model used to explain the behavior of polysaccharide-fatty acid films on WVP (Koelsch and Labuza, 1992; Koelsch, 1994), a protein-lipid interfacial interaction was proposed. These researchers hypothesized that immobilization of proteins at the lipid interface in emulsified films was responsible for the decrease in WVP observed with decreasing particle diameters, which resulted in increasing interfacial areas. Therefore, by controlling lipid particle size and distribution in emulsified films and coatings, moisture loss, respiration and oxidation in foods may be regulated.

WVP of WPI emulsified films produced with a wide range of lipid concentration (10–90% lipid) was investigated by Shellhammer and Krochta (1997b). Barrier properties of high-melting anhydrous milk-fat fractions were also compared with several high-melting waxes. Results showed that a significant reduction in WVP of WPI films could be achieved using large volume fractions of lipid depending on lipid type. In this study, emulsified films could be produced with up to 80% lipid level, but the carnauba and candelilla wax emulsified films cracked during drying when lipid levels were greater than 40%. The WVPs of the BW and milkfat emulsified films were significantly lower than those of films from carnauba and candelilla wax. For BW and a high-melting anhydrous milkfat fraction, a critical concentration existed at which a sharp reduction in film WVP occurred. However, the highest lipid particle size was observed in beeswax emulsified films while similar particle sizes were found in emulsified films with the other lipids. The researchers concluded that lipid WVP and degree of viscoelasticity instead of the lipid particle size determined the barrier properties of the films.

In another study conducted by Fairley *et al.* (1997), the interfacial interaction between whey protein and lipid (triolein or tripalmitin/butterfat blend) in WPI-lipid emulsified films was studied. According to their results, the interfacial interactions were small in triolein films and were not detected in tripalmitin/butterfat films. The physical state of the dispersed phase did not affect WVP. However, the distribution of the lipid droplets within the film was the primary determinant of WVP in the system studied.

The discrepancy in the effect of particle size may be related to the limitation of the technique used to obtain the particle size data. Laser light scattering was used in these studies. The limitation of using this instrument is that measurement needs to be done on the undried emulsion or the solution used to dissolve the film (Sherwin *et al.*, 1998). A new technique, light microscopy digital image analysis (DIA), can analyze particle size data directly from a dried and set film and has been introduced to use on edible films. Sherwin *et al.* (1998) used this method to study the effect of fatty acid type (saturated fatty acid C_{14} to C_{22}) on dispersed phase particle size distributed in emulsified WPI-fatty acid films. They reported that particle size increased with increasing chain length and found at least two populations of particles in the films which may reflect differences in the crystal formation during drying of the films. Their observation may be useful to explain functional property differences in future experiments.

Water vapor permeabilities of some protein-lipid multicomponent edible films can be found in Table IV.

B. OXYGEN BARRIER PROPERTIES

At the present time, less information is available on the O_2 permeability of protein-based multicomponent films compared to data on WVP. Results from one of the Gennadios and coworkers' studies on a wheat gluten film showed that adding a small amount of mineral oil to the film solution did not change the WVP of the wheat gluten film but WVP of both films were low (Gennadios *et al.*, 1993b). However, incorporation of AM into the wheat gluten film produced a plasticized gluten-AM film with 30% lower O_2 permeability in another study (Gennadios *et al.*, 1993c).

O_2 permeability of wheat gluten multicomponent films was tested by Gontard *et al.* (1996). At high RH (91%), O_2 permeability was reduced by about 30% in a gluten-BW (20%) emulsified film. At even higher RH (94%), including 30% of DTEM in the wheat gluten formulation, O_2 permeability was decreased by about 40%. As discussed in the water barrier properties of protein-lipid films section, these results are attributed to the increased hydrophobicity of the composite films. It was also previously demonstrated that DTEM has the ability to strengthen the protein structural matrix, thus improving the barrier properties of the film (Gontard *et al.*, 1992). In the same study, O_2 permeabilities of two laminated wheat gluten-lipid films were also tested. At 56% RH, very low O_2 permeabilities were observed for BW coated gluten-BW laminated films and BW coated gluten-DTEM laminated films. However, O_2 permeabilities of the two films at higher RH were not testable because the gluten-based film swelled with water absorption and separated from the BW layer.

O_2 permeabilities of a WPI film and a WPI-BW emulsified film were also examined by McHugh and Krochta (1994e). The addition of BW to WPI films resulted in significantly increased O_2 permeability while O_2 permeability of both films was lower than those of LDPE and HDPE (high density polyethylene) and comparable to those of ethylene vinyl alcohol films.

A summary of these data is given in Table III.

TABLE IV

WATER VAPOR PERMEABILITIES (WVP)^a OF PROTEIN-LIPID MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP (g·mm/m^2·d·KPa)	l (mm)	T (°C)	RH (%)	Reference
NaCaseinate		36.72^b	0.083	25	0–81	Avena-Bustillos & Krochta (1993)
	NaCaseinate:AM (1:0.2)	25.44^b	0.094	25	0–88	
	NaCaseinate:BW (1:0.25)	9.84^b	0.104	25	0–95	
	NaCaseinates:SA (1:0.2)	16.8^b	–	25	–	
CaCaseinate		28.08	0.082	25	0–84	
	CaCaseinate:BW (1:0.38)	6.72	0.075	25	0–97	
WG:Gly (2.5:1)		4.83	0.127	23	0–11	Gennadios *et al.* (1993b)
	WG:Gly:MO (2.5:1:0.58)	3.53	0.125	23	0–11	
WG:Gly (2.5:1)		4.83	0.101	23	0–11	Gennadios *et al.* (1993c)
	WG:AM (2.5:1:0.75)	4.83	0.066	23	0–11	
WG:Gly (5:1)		7.85	0.05	30	0–100	Gontard *et al.* (1994)
	WG:Gly:BW (5:1:1.5)	3.67	0.05	30	0–100	
	WG:Gly:DTEM (5:1:1.5)	3.70	0.05	30	0–100	
	BW//WG:Gly (1.3 mg·cm^{-2}//5:1)	3.08	0.05	30	0–100	Gontard *et al.* (1995)
	BW//WG:Gly:DTEM (1.3 mg·cm^{-2}//5:1:1.5)	1.91	0.05	30	0–100	
	BW//WG:Gly:DTEM (5.3 mg·cm^{-2}//5:1:1.5)	0.036	0.05	30	0–100	
	MG//WG:Gly:DTEM (53 mg·cm^{-2}//5:1:1.5)	0.74	0.05	30	0–100	

TABLE IV *(continued)*

WATER VAPOR PERMEABILITIES (WVP)[a] OF PROTEIN-LIPID MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP (g·mm/m²·d·KPa)	*l* (mm)	*T* (°C)	RH (%)	Reference
WPI:Sor (1.6:1)		61.92[b]	0.129	25	0–79	McHugh *et al.* (1994)
	WPI:Sor:MA (3.5:1.8:1)	23.76[b]	0.27	25	0–95	McHugh & Krochta (1994c)
	WPI:Sor:PA (3.5:1.8:1)	19.2[b]	0.14	25	0–93	
	WPI:Sor:BW (3.5:1.8:1)	20.4[b]	0.170	25	0–94	
	WPI:Sor:TET (3.5:1.8:1)	50.88[b]	0.20	25	0–88	
	WPI:Sor:SAL (3.5:1.8:1)	46.32[b]	0.15	25	0–86	
WPI:Gly (15:1)		45.4[b]	0.15	26.3	0–88	Shellhammer & Krochta (1997b)
	WPI:Gly:CARW (15:1:10.7)	33[b]	0.15	25	0–100	
	WPI:Gly:CANW (15:1:10.7)	30.98[b]	0.15	25	0–100	
	WPI:Gly:MF (15:1:10.7)	21.89[b]	0.15	25	0–100	
	WPI:Gly:BW (15:1:10.7)	10.82[b]	0.15	25	0–100	
SPI:Gly (5:2.5)		3.02[b]	0.635	25	50–100	Rhim *et al.* (1999a)
	SPI:Gly:Lecithin:LA (5:2.5:0.15:1.5)	1.92[b]	0.778	25	50–100	
	SPI:Gly:Lecithin:PA (5:2.5:0.15:1.5)	1.39[b]	0.825	25	50–100	
	SPI:Gly:Lecithin:SA (5:2.5:0.15:1.5)	1.49[b]	0.80	25	50–100	
	SPI:Gly:Lecithin:OA (5:2.5:0.15:1.5)	2.69[b]	0.856	25	50–100	

[a] Measured using standard methods; [b]measured using the WVP Correction Method (McHugh *et al.*, 1993; Gennadios *et al.*, 1994a). "·" = emulsion film; AM = acetylated monoglyceride; BW = beeswax; CANW = candelilla wax; CARW = carnauba wax; CaCaseinate = calcium caseinate; DTEM = diacetyl tartaric ester of monoglyceride; Gly = glycerol/glycerin; *l* = thickness; MA = myristic acid; MF = milkfat fraction; MG = monoglyceride; MO = mineral oil; PA = palmitic acid; SA = stearic acid; SAL = stearyl alcohol; NaCaseinate = sodium caseinate; Sor = sorbitol; SPI = soy protein isolate; *T* = temperature during transfer; TET = tetradecanol; WG = wheat gluten; WP = whey protein isolate; RH = relative humidity gradient.

C. FACTORS AFFECTING BARRIER PROPERTIES

1. RH

It was observed that the WVP of WPI films increased exponentially as RH increased (McHugh and Krochta 1994c), but this exponential effect of RH on WVP was substantially reduced in the WPI-BW (16%) emulsified films due to the increased hydrophobicity in the WPI films. The percentage reduction in WVP through the addition of beeswax was greater at high RHs than at low RHs.

Reduction in O_2 permeabilities in wheat gluten films has been observed by Gontard *et al.* (1996), as aforementioned, in wheat gluten-lipid multicomponent films. This reduction was also more pronounced at high RHs than at low RHs.

No data exists concerning the influence of temperature on the barrier properties of protein-based multicomponent films at this time.

2. Application of protein-lipid films

An edible coating produced by combining corn zein with special vegetable oils has been reported as an O_2 and moisture barrier (Andres, 1984). Currently, this coating is available commercially with a trade name Z*Coat (previously Cozeen, Zumbro, Inc., Hayfield, MN). It can be used to coat nutmeats, gummy bears, chocolate-covered peanuts and licorice candy, or used as carriers for antioxidants. Z*Coat could significantly extend shelf life of pecans to three months for storage at room temperature and 50% RH compared to uncoated pecans (Anon., 1997).

Avena-Bustillos *et al.* (1993) used response surface methodology to optimize a sodium caseinate-stearic acid emulsified coating formulation to maintain the quality of minimally processed carrots. According to their results, the storage stability of peeled carrots can be improved with an optimized 1.4~1.6% sodium caseinate with 0.1~0.2% SA emulsified coating formulation. Carrots sprayed with this formulation had minimum whitish blush (dried appearance), which is a major factor reducing consumer acceptance of minimally processed carrot products, during 10 days of storage in LDPE bags at 10°C.

Similar methodology also was used by Avena-Bustillos and Krochta (1994) to optimize a formulation of calcium caseinate-AM aqueous emulsion to reduce water loss in zucchini. Their results showed that uniform surface covering was enhanced by the surfactant properties of calcium caseinate, resulting in increased water vapor resistance at relative high caseinate and low AM content in edible coatings for zucchini stored up to 20 days. Also, it was found that this coating was superior to the commercial Semperfresh coating, which did not increase water vapor resistance of zucchini in this study.

In a recent study, Stuchell and Krochta (1995) tested the effect of WPI and AM coatings on moisture loss and lipid oxidation under frozen conditions when coatings were applied on frozen king salmon. They found that coatings consisting of AM used alone or over protein coatings were effective in reducing moisture loss while WPI alone provided little moisture barrier property at frozen temperature.

V. OTHER TYPES OF MULTICOMPONENT EDIBLE FILMS

Besides the two types of basic multicomponent films, composite films of polysaccharide-protein, polysaccharide-polysaccharide, protein-protein, or polysaccharide and/or protein with food additives have been developed during the 1990s. These films' barrier properties, mainly WVP have been investigated by several research groups as discussed below. Interactions between the macromolecules, such as charge-charge electrostatic linkage and covalent cross-linking, are the mechanisms of film formation. Film functional properties should be improved not only by the strength of one material compensating for the weakness of another, but also by any synergistic effect between components. The resulting multicomponent film should be more stable to heat, ionic effects, RH or other conditions. In those multicomponent films with food additives, the functional properties of polysaccharides or proteins are more in the carrier properties rather than barrier properties. In this section, only films with antioxidants will be covered.

A. BARRIER PROPERTIES

Gennadios *et al.* (1993b, c) investigated the physical and barrier properties of protein-protein films by partially substituting wheat gluten with keratin (13.3% of gluten), corn zein (20% of gluten) or soy protein isolate (SPI, 30% of gluten). WVP and O_2 permeability of gluten-keratin films were 23% and 85% lower than that for the control gluten films, respectively (Gennadios *et al.*, 1993b). Films containing corn zein had significantly better water barrier properties than the control film by about 23% but did not have an improved O_2 permeability. Partial substitution of wheat gluten with soy protein resulted in about a 40% reduction in the O_2 permeability but not in WVP (Gennadios *et al.*, 1993c). Linkage formation between proteins may have contributed to the improved properties of the protein composite films.

Shih (1994) demonstrated the potential use of protein-propyleneglycol alginate (PGA) in improving film performance including water stability of multicomponent films by forming covalent complexes between PGA and soy protein. Also, the addition of a small amount of lauric acid into the mixture of soy protein-PGA substantially increased its water vapor resistance. But, the effect of PGA on properties of soy protein film has not been comprehensively tested.

The effect of cross-linking PGA with proteins and other polysaccharides on film properties including WVP has been further studied by Shih (1996). PGA has been known for its good film-forming properties as well as its cross-linking effect with amino acid groups in proteins and hydroxyl groups in starch or other polysaccharides (McDowell, 1970). As a result, WVP of multicomponent films containing pullulan-PGA or rice protein concentrate-pullulan-PGA were significantly reduced by the presence of a small amount of PGA (about 1.5% of total solid) under alkaline conditions. These films also maintained their integrity when soaked in water. Edible films of soy protein isolate with different levels of PGA were developed in a recent study (Rhim *et al.*, 1999b). WVP and water solubility of these composite films decreased by the addition of PGA up to 10%, but further addition of PGA increased values of these properties. These results suggest that the site of reaction with PGA on the protein chain may become saturated with PGA at the 10% level.

Milk-based materials, whole milk, sodium caseinate, whey and nonfat dry milk have been incorporated into three acidic polysaccharide films, which were alginate, low methoxyl pectin (26% methoxyl ester) and high methoxyl pectin (70% methoxyl ester) films, in a study conducted by Parris *et al.* (1995), in order to improve WVP of the polysaccharide base films. All milk-based materials were found to significantly reduce the WVP of the hydrophilic base films by about 35% though no differences were found in WVP values for films containing different milk-based materials. Of the three different hydrocolloids tested, alginate films containing whole milk had the lowest WVP values. The charge-charge electrostatic complex formed between acidic polysaccharides and proteins may have contributed to these improved film properties.

Blends of sodium caseinate and corn starch were first used for preparing edible films by Arvanitoyannis *et al.* (1996). When plasticized with water at 15% level, the WVP of the composite films decreased proportionally from 6.29 to 4.65 $g{\cdot}mm/m^2{\cdot}d{\cdot}KPa$ with an increase in sodium caseinate contents (0% to 40% w/w). The gas permeability values of the composite films were also decreased as sodium caseinate contents increased. The less hydrophilic nature of the sodium caseinate compared to corn starch may contribute to the better barrier properties of these composite films. In this study, development of crystallinity within the film structure over time was also observed, which caused a reduction in gas and water permeabilities. However, high plasticizer level decreased the percentage of crystallinity, thus increasing the permeabilities.

Psomiadou *et al.* (1996) also developed edible films made from microcrystalline cellulose (MCC), MC and corn starch. They reported that high MCC or MC contents in aqueous starch/cellulose composite films resulted in lower WVPs and gas permeabilities. This could be due to the structure differences between starch and cellulose so that starch sorbs more water than cellulose (French, 1984). The up to 20% recorded crystallinity after 60 days storage resulted in lower permeability values by 3–4 magnitude orders in the composite films. However, it was also observed that the incorporation of MC resulted in a greater increase in WVP than that of MCC because of the higher flexibility and swelling capacity of MC compared to MCC.

Table V presents water vapor permeabilities of some of these multicomponent edible films. Oxygen permeabilities of some of these multicomponent edible films can be found in Table III.

B. APPLICATION OF OTHER TYPES OF MULTICOMPONENT EDIBLE FILMS

Little information is available on the applications of other types of multicomponent edible films as mass transfer barriers. However, one interesting basic application study has been reported by the scientists at USDA's Western Regional Research Center (Pavlath *et al.*, 1993). In this study, the three types of biopolymers were combined together to create a coating for a cut apple. The coating was an aqueous emulsion consisting of casein as an emulsifier, AM as a moisture barrier and alginate providing an interface, or cross-linking, between the hydrophilic cut surface and the hydrophobic lipid layer. Figure 4 shows how all these three components play a major role in the coating to control the moisture loss and discoloration of the apple for up to four days.

On the other hand, a few studies on the use of multicomponent films containing antioxidants on food systems have been reported. Tocopherols have been incorporated into gelatin films, starch-alginate coatings and AM coatings and used to protect margarine from lipid oxidation (Guilbert, 1988), to retard the formation of warmed-over flavor (WOF) in precooked pork chops (Hargens-Madsen *et al.*, 1995) and to delay the oxidative rancidity of walnuts (Mate and Krochta, 1997), respectively. Tocopherols have also been incorporated into or coated onto films of starch-alginate and starch-alginate-stearic acid to inhibit lipid oxidation in precooked ground beef patties (Wu *et al.*, 2001b). Ascorbyl palmitate has also been

TABLE V

WATER VAPOR PERMEABILITIES (WVP)^a OF OTHER TYPES OF MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP (g·mm/m^2·d·KPa)	l (mm)	T (°C)	RH (%)	Reference
WG:Gly (2.5:1)		4.83	0.127	23	0–11	Gennadios *et al.* (1993a)
	WG:Gly:Keratin (2.5:1:0.33)	3.71	0.125	23	0–11	
WG:Gly (2.5:1)		4.83	0.101	23	0–11	Gennadios *et al.* (1993b)
	WG:Gly:SPI (2.5:1:0.75)	4.40	0.08	23	0–11	
	WG:Gly:Zein (2.5:1:0.75)	3.70	0.072	23	0–11	
Alginate:Gly (2.3:1)		2.35^b	0.07	30	0–100	Parris *et al.* (1995)
	Alginate:Gly:WM (2.5:1:1.5)	1.66^b	0.06	30	0–100	
HM-pectin:Gly (2.3:1)		2.93^b	0.07	30	0–100	
	HM-pectin:Gly:WM (2.5:1:1.5)	1.94^b	0.06	30	0–100	
LM-Pectin:Gly (2.3:1)		3.19^b	0.07	30	0–100	
	LM-Pectin:Gly:WM (2.5:1:1.5)	2.18^b	0.06	30	0–100	
	LM-Pectin:LacA//Chitosan:LacA (2:1:1:1)	2.36^b	0.13	25	0–50	
Starch:water(5.7:1)		6.29	0.050	25	23–84	Arvanitoyannis *et al.* (1996)
	NaCasein:starch:water (3:2.7:1)	1.81	0.05	25	23–84	
Pullulan:PEG:Gly (24:1:2)		9.16	0.003	21	0–65	Shih (1996)
	Pullulan:PEG:Gly:PGA (24:1:2:0.4)	6.19	0.003	21	0–65	
	RP: Pullulan:PEG:Gly (10.28:13.72:1:2)	8.78	0.005	21	0–65	
	RP:Pullulan:PEG:Gly:PAG (10.28:13.72:1:2:0.4)	7.30	0.005	21	0–65	

TABLE V *(continued)*

WATER VAPOR PERMEABILITIES (WVP)[a] OF OTHER TYPES OF MULTICOMPONENT EDIBLE FILMS

Base film	Composite film	WVP (g·mm/m^2·d·KPa)	l (mm)	T (°C)	RH (%)	Reference
	RP:Pullulan:PEG:Gly (18.68:5.32:1:2)	12.50	0.01	21	0–65	
	RP:Pullulan:PEG:Gly:PAG (18.68:5.32:1:2:0.4)	8.72	0.01	21	0–65	
SPI:Gly (5:2.5)		$2.12^{\dagger\dagger}$	0.063	25	50–100	Rhim *et al.* (1999b)
	SPI:Gly:PGA (5:25:0.5)	$1.72^{\dagger\dagger}$	0.064	25	50–100	

[a] Measured using standard methods; [b]measured using the WVP Correction Method (McHugh *et al.*, 1993; Gennadios *et al.*, 1994a). "·" = emulsion film; "//" = coated or laminated onto = bilayer; HM = high methoxyl; LM = low methoxyl; Gly = glycerol; l = thickness; Na caseinate = sodium caseinate; PEG = polyethylene glycol/glycerin; RP = rice protein; SPI = soy protein isolate; T = temperature during transfer; WG = wheat gluten; WM = whole milk; RH = relative humidity gradient.

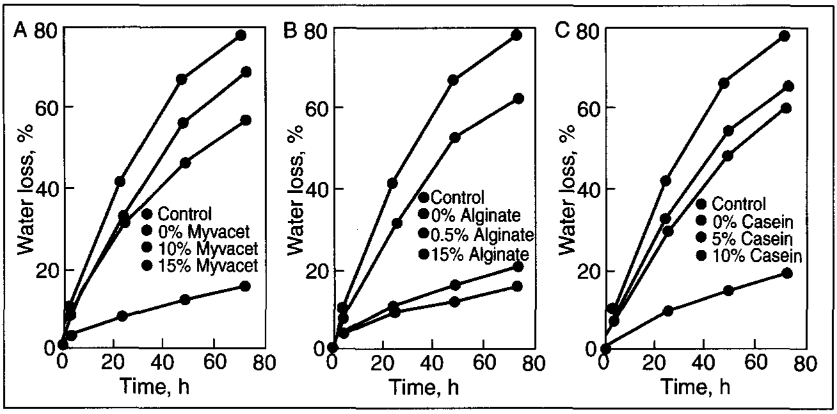

FIG. 4. Effect of coating composition on water loss of a cut apple. The apple sample is a cylinder 20 mm diameter and 20 mm high coated with emulsions containing varying amount of alginate of acetylated monoglyceride (Myvacet). (a) 10% casein, 1% alginate, and 0–15% Myvacet; (b) 10% casein, 15% Myvacet, 0–1% alginate; (c) 15% Myvacet, 1% alginate, and 0–10% casein. (Adapted from Pavlath *et al.*, 1993.)

added to AM coatings to inhibit the oxidative rancidity of walnuts (Mate and Krochta, 1997). Rosemary oleoresin, an oleoresin extract of spice with antioxidant activity, has been added into starch-alginate coatings to inhibit the lipid oxidation and WOF development in precooked pork chops (Handley *et al.*, 1997) and beef patties (Ma-Edmonds *et al.*, 1995). Whey protein isolate coatings with antioxidants (citric acid and ascorbic acid) overspray delayed the onset of lipid oxidation and reduced the peak peroxide values in frozen king salmon (Stuchell and Krochta, 1995). A corn zein film with butylated hydroxyanisole (BHA) has been reported to control the lipid oxidation in precooked turkey breast (Herald *et al.*, 1996).

VI. SUMMARY

Combining the advantages of polysaccharides, proteins and/or lipids offers multicomponent edible films and coatings good mass transfer barrier properties. Multicomponent edible films and coatings could be beneficial to the food industry by leading to innovative applications. The barrier properties of these systems strongly depend upon their structure and chemistry, the interaction between different film components as well as surrounding environment conditions. Future researches on these multicomponent systems need to concentrate on the following goals: (1) investigation of the optimal film compositions and specific film-forming conditions for different food systems; (2) study of the film responses in their barrier properties to environmental factors such as RH and temperature; (3) fundamental research of the mechanism of mass transfer and the interaction of different films components and foods; (4) exploration of the feasibility of potential applications in the food industry.

VII. LIST OF ABBREVIATIONS

AA:	arachidic acid (C_{22})
AM:	acetylated monoglycerides
BHA:	butylated hydroxyanisole
BW:	beeswax
CO_2:	carbon dioxide
D:	constant diffusion coefficient
DTEM:	diacetyl tartaric ester of monoglycerides
EC:	ethylcellulose
EA:	elaidic acid, $C_{18:1}$, *trans*
GM:	glycerol monostearate
HDPE:	high density polyethylene
HPMC:	hydroxypropyl methylcellulose
HPO:	hydrogenated palm oil
LA:	lauric acid (C_{14})
LDPE:	low density polyethylene
MA:	myristic acid (C_{14})
MC:	methylcellulose
MCC:	microcrystalline cellulose
OA:	oleic acid ($C_{18:1}$, *cis*)
O_2:	oxygen
P:	permeant
PA:	palmitic acid (C_{16})
PGA:	propyleneglycol alginate
PSP:	potassium sorbate permeability
PW:	paraffin wax
PVC:	polyvinyl chloride
RH:	relative humidity
S:	Solubility coefficient
SA:	stearic acid (C_{18})
SEM:	scanning electron microscopy
SP:	a blend of stearic acid and palmitic acid

SPI:	soy protein isolate
WOF:	warmed over flavor
WPI:	whey protein isolate
WS:	water solubility
WVP:	water vapor permeability

REFERENCES

Andres, C. 1984. Natural edible coating has excellent moisture and grease barrier properties. *Food Processing*. **45**, 48–49.

Anonymous. 1997. Edible films solve problems. *Food Technol.* **51** (2), 60.

Arvanitoyannis, I., Psomiadou, E., and Nakayama, A. 1996. Edible films made from sodium caseinate, starches, and sugars or glycerol. Part 1. *Carbohydr. Polym.* **31**, 179–192.

Avena-Bustillos, R.J., Krochta, J.M., Buhlert, J.E., Davila, G. 1990. Water vapor permeability of casein-acetylated monoglyceride edible films. Presented before Institute of Food Technologists Annual Meeting, Anaheim, 16–20 June.

Avena-Bustillos, R.J., and Krochta, J.M. 1993. Water vapor permeability of caseinate-based edible films as affected by pH, calcium crosslinking and lipid content. *J. Food Sci.* **58**, 904–907.

Avena-Bustillos, R.J., Cisneros-Zevallos, L.A., Krochta, J.M., and Saltveit, M.E. 1993. Optimization of edible coatings on minimally processed carrots using response surface methodology. *Trans. ASAE* **36**, 801–805.

Avena-Bustillos, R.J., and Krochta, J.M. 1994. Optimization of edible coating formulations on zucchini to reduce water loss. *J. Food Eng.* **21**, 197–214.

Baldwin, E.A. 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. Ch. 2 *in* "Edible Coatings And Films To Improve Food Quality" (M. Krochta, E.A. Baldwin and M. Nisperos-Carriedo, eds), pp. 25–64. Technomic Publishing Co., Inc., Lancaster, Basel.

Banker, G.S. 1966. Film coating – theory and practice. *J. Pham. Sci.* **55**, 81–89.

Banks, N.H. 1984. Some effects of TAL Pro-long coating on ripening bananas. *J. Exp. Bot.* **35**, 127–137.

Callegarin, F., Gallo, J-A.Q., Debeaufort, F., and Voilley, A. 1997. Lipids and biopackaging. *J. Am. Oil Chem. Soc.* **74**, 1183–1192.

21 CFR 184. Direct food substances affirmed as generally recognized as safe. Code of Federal Regulations, part 184, US GPO: Washington, DC, 1988, p. 404.

Cuppett, S. L. 1994. Edible coatings as carriers of food additives, fungicides and natural antioxidants. Ch. 6 *in* "Edible Coatings and Films to Improve Food Quality" (J. M. Krochta, E. A. Baldwin, and M. Nisperos-Carriedo eds), pp. 121–137. Technomic Publishing Company, Inc., Lancaster, PA.

Cuq, B., Gontard, N., and Guilbert, S. 1995. Edible films and coatings as active layers. Ch. 5 *in* "Active Food Packaging" (M. Rooney ed.), pp. 111–142. Blackie Academic and Professional, London.

Debeaufort, F., Martin-Polo, M., and Voilley, A. 1993. Polarity homogeneity and structure affect water vapor permeability of model edible films. *J. Food Sci.* **58**, 426–434.

Debeaufort, F., and Voilley, A. 1995. Effect of surfactants and drying rate on barrier properties of emulsified edible films. *Int. J. Food Sci. Technol*. **30**, 183–190.

Debeaufort, F., Quezada-Gallo, J-A., and Voilley, A. 1998. Edible films and coatings: tomorrow's packagings: a review. *Crit. Rev. Food Sci. Nutr.* **38**, 299–313.

Dhalla, R., and Hanson, S.W. 1988. Effect of permeability coatings on the storage life of fruits. II. Pro-long treatments of mangoes (*Mangifera indica* L. cv. Julie). *Int. J. Food Sci. Technol.* **23**, 107–112.

Donhowe, I.G., and Fennema, O. 1992. The effect of relative humidity gradient on water vapor permeance of lipid-hydrocolloid bilayer films. *J. Am. Oil Chem. Soc.* **69**, 1081–1087.

Donhowe, I.G., and Fennema, O. 1993. The effects of plasticizers on crystallinity, permeability, and mechanical properties of methylcellulose films. *J. Food Process. Preserv.* **17**, 247–257.

Drake, S.R., Fellman, J.K., and Nelson, J.W. 1987. Post-harvest use of sucrose polyesters for extending the shelf-life of stored 'Golden Delicious" apples. *J. Food Sci.* **52**, 1283–1285.

Fairley, P., Krochta, J.M., and German, J.B. 1997. Interfacial interactions in edible emulsion films from whey protein isolate. *Food Hydrocolloids.* **11**, 245–252.

French, D. 1984. Organization of starch granules. Ch. 7 *in* "Starch: Chemistry and Technology" (R.L. Whistler, J.N. Bemiller and E.F. Paschall, eds), pp. 184–247. Academic Press, New York.

Gennadios, A. and Weller, C.L. 1990. Edible films and coatings from wheat and corn proteins. *Food Technol.* **44**(10), 63–69.

Gennadios, A., Weller, C.L. and Testin, R.F. 1990. Modification of properties of edible wheat gluten films. ASAE Paper No 90–6504. St Joseph, MI, American Society of Agricultural Engineers.

Gennadios, A. and Weller, C.L. 1991. Edible films and coatings from soymilk and soy protein. *Cereal Food World* **36**, 1004–1009.

Gennadios, A., Brandenburg, A.H., Weller, C.L., and Testing, R.F. 1993. Effect of pH on properties of wheat gluten and soy protein isolate film. *J. Agric. Food Chem.* **41**, 1835–1839.

Gennadios, A., Park, H.J. and Weller, C.L. 1993a. Relative humidity and temperature effects on tensile strength of edible protein and cellulose ether films. *Trans. ASAE* **36**, 1867–1872.

Gennadios, A., Weller, C.L., and Testing, R.F. 1993b. Modification of physical and barrier properties of edible wheat gluten-based films. *Cereal Chem.* **70**, 426–429.

Gennadios, A., Weller, C.L., and Testing, R.F. 1993c. Properties modification of edible wheat gluten-based films. *Trans. ASAE* **36**, 465–470.

Gennadios, A., Weller, C.L., and Gooding, C.H. 1994a. Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films. *J. Food Eng.* **2**, 395–409.

Gennadios, A., McHugh, T.H., Weller, C.L., and Krochta, J.M. 1994b. Edible coatings and films based on proteins. Ch. 9 *in* "Edible Coatings And Films To Improve Food Quality" (M. Krochta, E.A. Baldwin and M. Nisperos–Carriedo, eds), pp. 201–277. Technomic Publishing Co., Inc., Lancaster. Basel.

Gennadios, A., Hanna, M.A., and Kurth, L. B. 1997a. Application of edible coatings on meats, poultry and seafoods: a review. *Lebensm.-Wiss. u.-Technol.* **30**, 337–350.

Gennadios, A., Weller, C.L, and Hanna, M.A. 1997b. Soy protein/fatty acid films and coatings. *INFORM.* **8**, 622, 624.

Greener, I.K., and Fennema O. 1989a. Barrier properties and surface characteristics of edible, bilayer films. *J. Food Sci.* **54**, 1393–1399.

Glicksman, M. 1982. "Food Hydrocolloids". Vol. II. CRC Press, Boca Raton, FL.

Gontard, N., Guilbert, S., and Cuq, J.L. 1992. Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. *J. Food Sci.* **57**, 190–195, 199.

Gontard, N., Duchez, C., Cuq, J.L., and Guilbert, S. 1994. Edible composite films of wheat gluten and lipids: water vapor permeability and other physical properties. *Int. J. Food Sci. Technol.* **29**, 39–50.

Gontard, N., Marchesseau, S., Cuq, J-L., and Guilbert, S. 1995. Water vapor permeability of edible bilayer films of wheat gluten and lipids. *Int. J. Food Sci. Technol.* **30**, 49–56.

Gontard, N., Thibault, R., Cuq, B., and Guilbert, S. 1996. Influence of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. *J. Agric. Food Chem.* **44**, 1064–1069.

Greener, I.K. and Fennema, O. 1989a. Barrier properties and surface characteristics of edible, bilayer films. *J. Food Sci.* **54**, 1393–1399.

Greener, I.K. and Fennema, O. 1989b. Evaluation of edible, bilayer films for use as moisture barriers for food. *J. Food Sci.* **54**, 1400–1406.

Guilbert, S. 1986. Technology and application of edible protective films. *In* "Food Packaging and Preservation. Theory and Practice" (Mathlouthi, M., ed.), pp. 371–394. Elsevier Applied Science Publishers, New York.

Guilbert, S. 1988. Use of superficial edible layer to protect intermediate moisture foods: Application to the protection of tropical fruit dehydrated by osmosis. *In* "Food Preservation by Moisture Control" (C.C. Seow, T.T. Teng, and C.H. Quah, eds), pp. 199–220. Elsevier Applied Science, New York.

Guilbert, S., Gontard. N., and Gorris, L.G.M. 1996. Prolongation of the shelf–life of perishable food products using biodegradable films and coatings. *Lebensm.-Wiss. u.-Technol.* **29**, 10–17.

Hagenmaier, R.D. and Shaw, P.E. 1990. Moisture permeability of edible films made with fatty acid and (hydroxypropyl)methyl-cellulose. *J. Agric. Food Chem.* **38**, 1799–1803.

Handley, D., Ma-Edmonds, M., Hamouz, F., Cuppett, S., Mandigo, R., and Schnepf, M. 1997. Controlling oxidation and warmed-over flavor in precooked pork chops with rosemary oleoresin and edible film. Ch. 19 *in* "Natural Antioxidants Chemistry, Health Effect, and Application" (F. Shahidi, ed.), pp. 311–318. AOCS Press, Champaign, IL.

Hanlon, J.F. (ed.). 1992. Films and foils. *In* "Handbook of Package Engineering", pp. 3.1–3.59. Technomic Publishing Co., Inc., Lancaster. Basel.

Hargens-Madsen, M., Schnepf, M., Hamouz, F., Weller, C., and Roy, S. 1995. Use of edible films and tocopherols in the control of warmed-over flavor. *J. Am. Diet. Assoc.* **95**, A-41.

Herald, T. J., Hachmeister, K. A., Huang, S., and Bowers, J.R. 1996. Corn zein packaging materials for cooked turkey. *J. Food Sci.* **61**, 415–417, 421.

Kamper, S.L., and Fennema, O. 1984a. Water vapor permeability of edible bilayer films. *J. Food Sci.* **49**, 1478–1481.

Kamper, S.L., and Fennema, O. 1984b. Water vapor permeability of an edible, fatty acid, bilayer film. *J. Food Sci.* **49**, 1482–1484.

Kamper, S.L., and Fennema, O. 1985. Use of an edible film to maintain water vapor gradients in foods. *J. Food Sci.* **50**, 382–384.

Kester, J.J., and Fennema, O. 1986. Edible films and coatings: A review. *Food Technol.* **40**(12), 47–49.

Kester, J.J., and Fennema, O. 1989a. An edible film of lipids and cellulose ethers: Barrier properties to moisture vapor transmission and structural evaluation. *J. Food Sci.* **54**, 1383–1389.

Kester, J.J., and Fennema, O. 1989b. Resistance of lipid films to water vapor transmission. *J. Am. Oil Chem. Soc.* **66**, 1139–1146.

Kester, J.J., and Fennema, O. 1989c. The influence of polymorphic form on oxygen and water vapor transmission through lipid films. *J. Am. Oil Chem. Soc.* **66**, 1147–1153.

Kester, J.J., and Fennema, O., 1989d. An edible film of lipids and cellulose ethers: Performance in a model frozen-food system. *J. Food Sci.* **54**, 1390–1392.

Koelsch, C. 1994. Edible water vapor barriers: properties and promise. *Trends Food Sci. Technol.* **5**, 7681.

Koelsch, C.M., and Labuza, T.P. 1992. Functional, physical and morphological properties of methyl cellulose and fatty acid-based edible barriers. *Lebensm.-Wiss. u.-Technol.* **25**, 404–411.

Krochta, J.M., Pavlath, A.E. and Goodman, N. 1990. Edible films from casein-lipid emulsions for lightly processed fruits and vegetables. *In* "Engineering and Food' (W.E.L. Spiess and H. Schubert, eds). Elsevier Applied Science Publishers, New York.

Krochta, J.M. 1992. Control of mass transfer in foods with edible coatings and films. Ch. 39 in "Advances In Food Engineering" (R.P. Singh and M.A. Wirakaratakusumah, eds), pp. 517–538. CRC Press, Inc., Boca Raton, FL.

Krochta, J.M., and De Mulder-Johnston, C. 1997. Edible and biodegradable polymer films: challenges and opportunities. *Food Technol.* **51**(2), 61–72.

Lai, H-M., Padua, G.W., and Wei, L.S. 1997. Properties and microstructure of zein sheets plasticized with palmitic and stearic acids. *Cereal Chem.* **74**, 83–90.

Leman, J., and Kinsella, J.E. 1989. Surface activity, film formation, and emulsifying properties of milk proteins. *Crit. Rev. Food Sci. Nutr.* **28**, 115–138.

Ma-Edmonds, M., Hamouz, F., Cuppett, S., Mandigo, R., and Schnepf, M. 1995. Use of rosemary oleoresin and edible film to control warmed-over flavor in precooked beef patties. *In* "Book of Abstracts", Institute of Food Technologists, Chicago, IL, p. 139.

Martin-Polo, M., Maughuin, C. and Voilley, A. 1992. Hydrophobic films and their efficiency against moisture transfer. 1. Influence of the film preparation technique. *J. Agric. Food Chem.* **40**, 407–412.

Mate, J. I., and Krochta, J. M. 1997. Whey protein and acetylated monoglyceride edible coatings: effect on the rancidity process of walnuts. *J. Agric. Food Chem.* **45**, 2509–2513.

McDowell, R. H. 1970. New reactions of propylene glycol alginate. *J. Soc. Cosmet. Chem.* **21**, 441–457.

McHugh, T.H., and Krochta, J.M. 1994a. Milk-protein-based edible films and coatings. *Food Technol.* **48**(1), 97–103.

McHugh, T.H., and Krochta, J.M. 1994b. Permeability properties of edible films. Ch. 7 *in* "Edible Coatings and Films to Improve Food Quality" (J.M. Krochta, E.A. Baldwin and M.Nisperos-Carriedo, eds), pp. 139–187. Technomic Publishing Co., Inc., Lancaster, Basel.

McHugh, T.H., and Krochta, J.M. 1994c. Water vapor permeability properties of edible whey protein-lipid emulsion films. *J. Am. Oil Chem. Soc.* **71**, 307–312.

McHugh, T.H., and Krochta, J.M. 1994d. Dispersed phase particle size effects on the water vapor permeability of whey protein-beeswax edible emulsion films. *J. Food Process. Preserv.* **18**, 173–188.

McHugh, T.H., and Krochta, J.M. 1994e. Sorbitol-vs glycerol-plasticized whey protein edible films: Integrated oxygen permeability and tensile property evaluation. *J. Agric. Food Chem.* **42**, 841–845.

McHugh, T.H., Avena-Bustillos, R., and Krochta, J.M. 1993. Hydrophilic edible films: Modified procedure for water vapor permeability and explanation of thickness effects. *J. Food Sci.* **58,** 899–903.

McHugh, T.H., Aujard, J.-F., and Krochta, J.M. 1994. Plasticized whey protein edible films: water vapor permeability properties. *J. Food Sci.* **59**, 416–419, 423.

Meheriuk, M., and Lau, O.L. 1988. Effect of two polymeric coatings on fruit quality of 'Bartlett' and 'dAnjou' pears. *J. Am. Soc. Hort. Sci.* **113**, 222–226.

Miller, K. S. and Krochta, J. M. 1997. Oxygen and aroma barrier properties of edible films: A review. *Trends Food Sci. Technol.* **8**, 228–237.

Nisperos-Carriedo, M.O., Shaw, P.E., and Baldwin, E.A. 1990. Changes in volatile flavor components of pineapple orange juice as influenced by the application of lipid and composite films. *J. Agric. Food Chem.* **38**, 1382–1387.

Park, H.J., Bunn, J.M., Weller, C.L., Vergano, P.J., and Testin, R.F. 1994. Water vapor permeability and mechanical properties of grain protein-based films as affected by mixtures of polyethylene glycol and glycerin plasticizers. *Am. Soc. Agric. Engineers* **37**, 1281–1285.

Park, H.J., and Chinnan, M.S. 1990. Properties of edible coatings for fruits and vegetables. ASAE paper No. 90-6510. St Joseph, MI, American Society of Agricultural Engineers.

Park, J.W., Testin, R.F., Park, H.J., Vergano, P.J., and Weller, C.L. 1994. Fatty acid concentration effect on tensile strength, elongation, and water vapor permeability of laminated edible films. *J. Food Sci.* **59**, 916–919.

Park, J.W., Testin, R.F., Vergano, P.J., Park, H.J., and Weller, C.L. 1996a. Fatty acid distribution and its effect on oxygen permeability in laminated edible films. *J. Food Sci.* **61**, 401–406.

Park, J.W., Testin, R.F., Vergano, P.J., Park, H.J., and Weller, C.L. 1996b. Application of laminated edible films to potato chip packaging. *J. Food Sci.* **61**, 766–768, 777.

Parris, N., Coffin, D.R., Joubran, R.F., and Ressen, H. 1995. Composition factors affecting the water vapor permeability and tensile properties of hydrophilic films. *J. Agric. Food Chem.* **43**, 1432–1435.

Pascat, B. 1986. Study of some factors affecting permeability. Ch. 2 *in* "Food Packaging and Preservation. Theory and Practice" (M. Mathlouthi, ed.), pp. 7–24. Elsevier Applied Science Publishers, New York.

Pavlath, A.E., Wong, D.S.W., and Kumosinski, T.F. 1993. New coatings for cut fruits and vegetables. *Chemtech.* **2**, 36–40.

Psomiadou, E., Arvanitoyannis, I., and Yamamoto, N. 1996. Edible films made from natural resources; microcrystalline cellulose (MCC, methylcellulose (MC) and corn starch and polyols – Part 2. *Carbohydr. Polym.* **31**, 193–204.

Rhim, J-W, Wu, Y., Weller, C.L., and Schnepf, M. 1999a. Physical characteristics of emulsified soy protein-fatty acid composite films. *Sci. Aliments* **19**, 57–71.

Rhim, J-W, Wu, Y., Weller, C.L., and Schnepf, M. 1999b. Physical characteristics of a composite film of soy protein isolate and propyleneglycol alginate. *J. Food Sci.* **64**, 149–152.

Rico-Pena, D.C., and Torres, J.A. 1990a. Oxygen transmission rate of an edible methylcellulose-palmitic acid film. *J. Food Process. Eng.* **13**, 125–133.

Rico-Pena, D.C., and Torres, J.A. 1990b. Edible methylcellulose-based films as moisture-impermeable barriers in sundae ice cream cones. *J. Food Sci.* **55**, 1468–1469.

Rico-Pena, D.C., and Torres, J.A. 1991. Sorbic acid and potassium sorbate permeability of an edible methylcellulose-palmitic acid film: water activity and pH effect. *J. Food Sci.* **56**, 497–499.

Rouse, P.E. 1947. Diffusion of vapors in films. *J. Am. Chem. Soc.* **69**, 1068–1073.

Salame, M. 1986. Barrier polymers. *In* "The Wiley Encyclopedia of Packaging Technology" (M. Bakker, ed.), pp. 48–54. John Wiley & Sons. Inc., New York.

Sapru, V., and Labuza, T.P. 1994. Dispersed phase concentration effect on water vapor permeability in composite methyl cellulose-stearic acid edible films. *J. Food Process. Preserv.* **18**, 359–368.

Schultz, T.H., Miers, J.C., Owens, H.S., and Maclay, W.D. 1949. Permeability of pectinate films to water vapor. *J. Phys. Colloid Chem.* **53**, 1320–1330.

Shellhammer, T.H., and Krochta, J.M. 1997a. Edible coatings and film barriers. Ch. 17 *in* "Lipid Technologies and Applications" (F.D. Gunstone and F.B. Padley, eds), pp. 453–479. Marcel Dekker, Inc., New York.

Shellhammer, T.H., and Krochta, J.M. 1997b. Whey protein emulsion film performance as affected by lipid type and amount. *J. Food Sci.* **62**, 390–394.

Sherwin, C.P., Smith, D.E., and Fulcher, R.G. 1998. Effect of fatty acid type on dispersed phase particle size distributions in emulsion edible films. *J. Agric. Food Chem.* **46**, 4534–4538.

Shih, F.F. 1994. Interaction of soy isolate with polysaccharide and its effect on film properties. *J. Agric. Food Chem.* **71**, 1281–1285.

Shih, F.F. 1996. Edible films from rice protein concentrate and pullulan. *Cereal Chem.* **73**, 406–409.

Smith, S.A. 1986. Polyethylene, low density. *In* "The Wiley Encyclopedia of Packaging Technology" (M. Bakker, ed), p. 514–523. John Wiley & Son, New York.

Smith, S.M., and Stow, J.R. 1984. The potential of a sucrose ester coating material for improving the storage and shelf life qualities of Cox's Orange Pippin Apples. *Ann. Appl. Biol.* **104**, 383–391.

Snyder, H.E., and Kwon, T.W. 1987. "Soybean Utilization". Van Nostrand Reinhold, New York.

Stuchell, Y.M., and Krochta, D.L. 1995. Edible coatings on frozen King Salmon: Effect of whey protein isolate and acetylated monoglycerides on moisture loss and lipid oxidation. *J. Food Sci.* **60**, 28–31.

Taylor, C.C. 1986. Cellophane. *In* "The Wiley Encyclopedia of Packaging Technology" (M. Bakker, ed.), pp. 159–163. John Wiley & Son, New York.

Torres, J.A. 1987. Microstabilization of intermediate moisture food. Ch. 14 *in* "Water Activity: Theory and Practice" (L.B. Rockland and L.R. Beuchat, eds), pp. 329–368. Marcel Dekker, New York.

Torres, J.A., Motoki, M., and Katel, M. 1985. Microbial stabilization of intermediate moisture food surface I: Control of surface preservative concentration. *J. Food Process. and Preserv* **9**, 75–92.

Vojdani, F., and Torres, J.A. 1989. Potassium sorbate permeability of methylcellulose and hydroxypropyl methylcellulose multi-layer films. *J. Food Process. Preserv.* **13**, 417–430.

Vojdani, F., and Torres, J.A. 1990. Potassium sorbate permeability of methylcellulose and hydroxypropyl methylcellulose coatings, Effect of fatty acids. *J. Food Sci.* **55**, 841–846.

Ukai, N.Y., Shingo, I., Kurume, T.T. and Fukuoka, K.M. 1976. Preservation of agricultural products. U.S. Pat. 3,997,674. Dec. 14.

Wong, D. W. S., Gastineau, F. A., Gregorski, K. S., Tillin, S. J., and Pavlath, A. E. 1992. Chitosan-lipid films: Microstructure and surface energy. *J. Agric. Food Chem.* **40**, 540–544.

Wu, L.C. and Bates, R.P. 1972. Soy protein-lipid films. 1. Studies on the film formation phenomenon. *J. Food Sci.* **37**, 36–39.

Wu, Y., Weller, C.L., Hamouz, F., Cuppett, S.L., and Schnepf, M. 2000. Moisture loss and lipid oxidation for precooked ground beef patties stored in edible coatings and films. *J. Food Sci.* **65**, 300–304.

Wu, Y., Weller, C.L., Hamouz, F., Cuppett, S.L., and Schnepf, M. 2001a. Water permeability, water solubility and microstructure of emulsified starch-fatty acid composite films. *In* "Transport Phenomena in Food Processing" (G. Barbosa-Canovas, J. Velez-Ruiz and J. Welti-Chanes, eds), to be published. Technomic Publishing Co., Inc., Lancaster, PA.

Wu, Y., Weller, C.L., Hamouz, F., Cuppett, S.L., and Schnepf, M. 2001b. Moisture loss and lipid oxidation for precooked ground beef patties packaged in edible starch-alginate based films. *J. Food Sci.* **66**, 486–493.