Composition Factors Affecting the Water Vapor Permeability and Tensile Properties of Hydrophilic Films

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The water vapor permeability of hydrophilic films was decreased without significantly compromising the film's tensile properties through the incorporation of whole milk, sodium caseinate, nonfat dry milk, or whey into the film and the proper choice of plasticizer. Sodium alginate films exhibited lower water vapor permeability values than films prepared using either low or high methoxylated pectin. Sodium lactate was found to be an effective plasticizer, and alginate films containing 50 wt % or more sodium lactate had elongations in excess of 13%. Films prepared with sorbitol as the plasticizer had the best water vapor permeability values but tended to be stiff and in some cases too brittle for tensile measurements. Addition of whole milk to film blends effectively reduced water vapor permeability values by up to 35%.

Keywords: *Hydrophilic; film; milk-based material; plasticizer; water vapor permeability; tensile properties*

INTRODUCTION

Recently there has been renewed interest in the preparation of biopolymer films and coatings from polysaccharide, protein, and lipid materials. Such films alone or in combination have the potential to control mass transfer and thus extend food shelf life. A number of comprehensive review papers have been published on the use of edible films and coatings for food preservation (Guilbert, 1986; Kester and Fennema, 1986; Gennadios and Weller, 1990; McHugh and Krochta, 1994a). Edible films prepared from polysaccharides (e.g. starch and cellulose) and hydrocolloids (e.g. pectin, alginate, and carrageenan) form strong films but, because of their hydrophilic nature, exhibit poor water vapor barrier properties (Kester and Fennema, 1986; Guilbert, 1986). Edible bilayer films composed of hydroxypropylmethylcellulose and various lipid layers have water vapor permeabilities less than low-density polyethylene (Kamper and Fennema, 1984a,b; Hagenmaier and Shaw, 1990). Greener and Fennema (1989) examined the barrier properties of methylcellulose films coated with beeswax in a molten or ethanolic state. More recently, Park et al. (1993) evaluated barrier and mechanical properties of cellulose-based edible films prepared from celluloses of different molecular weights. They found that the film's tensile strength and oxygen and water vapor permeabilities increased with increasing molecular weight of the cellulose.

Edible films prepared from dried soluble protein, e.g., gelatin, casein, serum albumin, and egg albumin, also exhibit poor water vapor barrier properties (Guilbert, 1986). However, cross-linking these proteins with lactic acid, tannic acid, or ionized calcium has been shown to increase resistance to water vapor and gas transport (Kumins, 1965). Recently, McHugh and Krochta (1994a) indicated that milk-protein films have favorable barrier and mechanical properties which warrant further investigation. Treating sodium caseinate films with calcium ascorbate buffer (pH 4.6) reduced water permeability by approximately 40% (Avena-Bustillos and Krochta, 1993). In addition, films prepared from aqueous emulsions of calcium caseinate and beeswax exhibited a 90% reduction in water vapor permeability compared to calcium caseinate alone. The water vapor permeability of whey protein–lipid emulsion films was significantly reduced for films prepared with heat-denatured whey proteins and with fatty acid or alcohol of increasing chain length (McHugh and Krochta, 1994b). Edible films, intended as coating for lightly processed fruits and vegetables, have been prepared from aqueous emulsions of equal amounts of casein and acetylated monoglycerides. These films were found to exhibit half the water permeability of films made without lipids (Krochta et al., 1990). Thermal denaturation of whey proteins can improve the film's water vapor barrier properties (McHugh et al., 1994). Mahmoud and Savello (1992, 1993) found that covalently cross-linking whey proteins with transglutaminase resulted in stronger films which were significantly less water soluble. Chen et al. (1994) have shown that microfluidization and ultrasound treatments used during film formation improved the mechanical strengths and barrier properties of whey protein films.

In this study, film blends of various hydrocolloids (pectins or alginate), milk-based materials, and plasticizers were screened and evaluated for tensile and water vapor barrier properties. The objective of this research was to improve film water vapor barrier properties through the incorporation of butter fat from whole milk and the cross-linking of milk protein as well as the proper choice of plasticizer, without significantly compromising strength.

MATERIALS AND METHODS

Materials. *Hydrocolloids* used included the following: GENU pectin, LM104AS-YA, degree of esterification, 26% (Hercules Inc., Middletown, NY); Mexpectin, RS450 (Mexpec), min degree of esterification, 70%; and SOBALG FD 175 alginate (Grinsted Products, Inc., Industrial Airport, KS).

Milk Proteins. Nonfat dry milk (NDM) [36% protein, <1% butter fat (BF), 52% lactose], sodium caseinate (95% protein, <1% BF, 1% lactose), and whey (12% protein, <1% BF, 71% lactose) were prepared and isolated according to a previously published procedure (Parris et al., 1991). Whey was dialyzed

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at 4 °C against 6 L of water, changed four times over 48 h, and termed lactose-free whey. β-D-Lactose was obtained from Eastman Fine Chemicals (Rochester, NY). To avoid problems associated with batch variation of whole milk, simulated whole milk (SWM) was prepared by dissolving 10 g of low-heat NDM in 100 mL of water which was heated to 70 °C. The surfactant, monodiglyceride (mp 130 °F) (0.5 g), and BF (3.0 g) were added to the solution, which was homogenized with a Tekmar homogenizer (Tekmar, Co., Cincinnati, OH) for 5 min at 70% output.

Plasticizers included 85% glycerine (J. T. Baker Chemical Co., Phillipsburg, NJ), 85% lactic acid (Fisher Scientific, Pittsburgh, PA), which was adjusted to pH 5.6 with 1 N NaOH, and D-sorbitol (Sigma, St. Louis, MO).

Film Formation. The appropriate quantity of hydrocolloid was dissolved in water followed by the plasticizer and then protein, to yield a 1% (w/w) mixture. The mixture was then stirred until all of the solids were in solution. Samples were degassed to remove dissolved air. Solutions were cast in aluminum rings of 4-1/4 in. diameter, resting on a glass support surface, to maintain constant area and uniform thickness. Samples were allowed to dry for approximately 18 h at 25 ± 2 °C and then stored at 50 ± 5% relative humidity (RH) until testing.

Film Thickness Measurement. A micrometer (Tumico, St. James, MN) was used to measure film thickness. Reported thicknesses are the mean values of 10 random measurements.

Water Vapor Permeability (WVP) Determination. The apparatus and methodology described in the ASTM E96-80 (ASTM, 1980) "Water Method", as modified by McHugh et al. (1993), were used to measure the WVP of the films. Four replicates of each type were tested at 30 ± 2 °C. Air velocities were approximately 150 m/min across the films. Cast films were shiny in the side facing the glass plate surface. Films were sealed on Plexiglas cups containing 9 mL of distilled water with the shiny side positioned toward the water. There was an air gap of 0.6 cm between the water and the underside of the film. Test cups were placed in a desiccator cabinet maintained at 0% RH with calcium sulfate. Cups were weighed a minimum of five times at intervals no less than 3 h apart. The water vapor transmission rate was calculated from a linear regression of the slope of weight loss vs time. Water vapor transmission rate (WVTR) was calculated by dividing the slope by the test cell mouth area. Permeance [WVTR/($p_2 - p_3$)] was calculated at 30 °C as described by McHugh et al. (1993), where p_2 and p_3 are the corrected partial pressure at the inner surface of the film and at the film outer surface, respectively. Water vapor permeability was calculated as the product of the permeance and average thickness of the film.

Tensile Property Measurements. Mechanical testing was carried out on a Rheometrics RSA II solids analyzer (Piscataway, NJ) using a film testing fixture. Testing was done within 24 h of sample preparation. During this period samples were stored in an incubator at 25 °C ± 2 and RH of 50 ± 5%. Test samples were cut from the films with a razor blade. Nominal dimensions of the samples were 4.0 mm × 38.1 mm × 0.04 mm. The gap between the jaws at the beginning of each test was 23.0 mm. Data analysis was carried out using the Rheometrics RHIOS software. Three parameters were obtained from the stress–strain measurements, namely the initial modulus, the tensile strength (TS), and the elongation to break (ETB). Tensile data were obtained for five replicates at room temperature using a strain rate of 0.005 s^{-1} (30%/min). A maximum elongation of 13% could be obtained due to instrument constraints. Ambient humidity during testing was in the range of 30–50%.

RESULTS AND DISCUSSION

Initially, biopolymer blends of hydrocolloid, protein, and plasticizer were screened to encompass the widest variety of compositions. The films were qualitatively evaluated for brittleness, tackiness, strength, haziness, off-color, and graininess. In general, films were between 0.06 and 0.08 mm thick. Alginate films were generally clearer and smoother than films prepared using either of the two pectin hydrocolloids. At less than 10 wt % (based on total solids) plasticizer, films were brittle, whereas those above 25 wt % tended to become tacky. Of the proteins tested, casein formed the best films with respect to qualitative parameters, followed by NDM and whey, in reverse order of increasing lactose content.

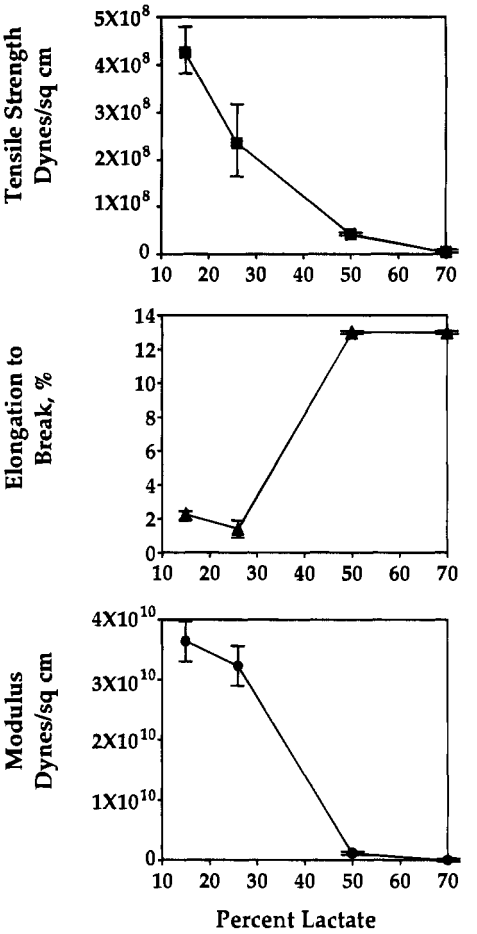

Figure 1. Effect of sodium lactate concentration on alginate film tensile properties: (■) tensile strength (TS); (▲) elongation to break (ETB); (●) modulus.

Table 1. Effect of Plasticizer Type on Alginate Film Tensile Properties[a]

plasticizer	TS (dyn/cm²)	CV[b]	ETB (%)	CV	modulus (dyn/cm²)	CV
glycerine	2.77E + 08a	15.13	4.86a	39.87	1.45E + 10c	7.27
sorbitol	2.14E + 08a	25.39	1.09b	31.16	2.78E + 10a	13.11
lactate	2.92E + 08a	27.74	3.18ab	55.61	2.13E + 10b	20.64

[a] Alginate/plasticizer 70/30 wt %. Values followed by different letters are significantly different at $p < 0.05$ using the Bonferroni lsd multiple-comparison method. [b] Coefficient of variation.

Tensile Properties. Three quantitative parameters were obtained from stress–strain measurements: tensile strength (TS), elastic modulus, and elongation to break (ETB). The most significant change in film tensile properties occurred with changes in plasticizer concentration. For example, increasing the amount of sodium lactate in alginate films decreased the film modulus and TS (Figure 1). Films containing 50 wt % or more sodium lactate did not break at elongations in excess of 13%. The effect of plasticizer type on alginate film tensile properties was examined for films composed of 70 wt % alginate and 30 wt % plasticizer (Table 1). Glycerine and sodium lactate plasticized films were stronger and more elastic than those prepared with sorbitol, as indicated by their TS and ETB values. In

Table 2. Effect of Hydrocolloid Type on Glycerine Plasticized Film Tensile Properties[a]

hydrocolloid	TS (dyn/cm²)	CV	ETB (%)	CV	modulus (dyn/cm²)	CV
alginate	2.99E + 08a	19.69	7.87a	45.65	1.47E + 10a	17.34
Mexpec	3.20E + 08a	26.05	7.36a	57.35	1.58E + 10a	14.56
pectin	1.11E + 08b	20.49	5.00a	50.92	0.44E + 10b	21.33

[a] Hydrocolloid/glycerine 70/30 wt %. Values followed by different letters are significantly different at of $p < 0.05$ using the Bonferroni lsd multiple-comparison method.

Table 3. Water Vapor Permeability of Hydrocolloid Films

film type[a]	WVP[b] (g mm/kPa h m²) glycerine	lactate	sorbitol
alginate	2.35 ± 0.05c	2.07 ± 0.14c	1.19 ± 0.09d
Mexpec	2.93 ± 0.19b	3.00 ± 0.15b	1.42 ± 0.10d
pectin	3.19 ± 0.16b	3.65 ± 0.22a	1.45 ± 0.12d

[a] 70 wt % hydrocolloid/30 wt % plasticizer (2.3:1). [b] WVP values corrected for stagnant air effects, at 30 °C, according to modified ASTM E96 Standard Method, McHugh et al. (1993). Values followed by different letters are significantly different at $p < 0.05$ using the Bonferroni lsd multiple-comparison method.

Table 4. Water Vapor Permeability, Thickness, and Relative Humidity of Glycerine Plasticized Milk-Based Films

film type	thickness (mm)	RH[a] (%)	WVP[b] (g mm/kPa h m²)
hydrophilic[c]			
no protein	0.0736	76.8	2.66 ± 0.20a
whey	0.0688	80.5	1.93 ± 0.14b
casein	0.0681	81.7	1.76 ± 0.11b
NDM	0.0635	79.4	1.92 ± 0.12b
whole milk	0.0631	80.4	1.77 ± 0.14b
synthetic[d]			
polyethylene	0.0078	99.8	0.0022
poly(vinylidene chloride)	0.0084	99.8	0.0016

[a] Relative humidity at the inner surface of the film. [b] Corrected for stagnant air effects. Values followed by different letters are significantly different at $p < 0.05$ using the Bonferroni LSD multiple-comparison method. [c] Alginate 50 wt %/30 wt % milk-based material/20 wt % glycerine (2.5:1). [d] Commercial films.

Table 5. Water Vapor Permeability of Hydrocolloid/ Simulated Whole Milk Films

film type[a]	WVP[b] (g mm/kPa h m²) glycerine	lactate	sorbitol
alginate	1.66 ± 0.08e	1.76 ± 0.04de	1.13 ± 0.09g
Mexpec	1.94 ± 0.12cd	2.28 ± 0.04b	1.40 ± 0.02f
pectin	2.18 ± 0.14bc	2.93 ± 0.16a	1.31 ± 0.09fg

[a] 50 wt % hydrocolloid/30 wt % SWM/20 wt % plasticizer. [b] Values followed by different letters are significantly different at $p < 0.05$ using the Bonferroni lsd multiple-comparison method.

addition, sorbitol films tended to be stiffer than the other films tested. The effect of hydrocolloid type on film tensile properties containing 30 wt % glycerine (Table 2) indicated that alginate and Mexpec films were stronger and tended to be more stiff than pectin films. However, no significant difference in flexibility was observed among the three types of films.

Water Vapor Barrier Properties. Water vapor permeability was compared for film blends of three different hydrocolloids and three different plasticizers using the method modified by McHugh et al. (1993) (Table 3). Alginate films exhibited better water vapor barrier properties than either of the two types of pectin films. At the same plasticizer concentration, sorbitol films exhibited better barrier properties than either the lactate or glycerine films. It appears that sorbitol is less effective in reducing intermolecular hydrogen bonding between polymer molecules compared to the other plasticizers. As a result, spacing between macromolecules is decreased, resulting in a reduction in WVP but an increase in the stiffness, a decrease in the strength, and a decrease in the elongation of the sorbitol films (compare Tables 1 and 3).

Effect of Milk-Based Materials. In an effort to improve the barrier properties of hydrocolloid films and not compromise their tensile properties, addition of milk-based material was investigated. At the same sodium lactate concentration, film tensile strength decreased with increasing concentration of whey and casein (compare parts a and b of Figure 2). At whey concentrations less than 10 wt %, there was relatively little change in the TS of the film. However, above this concentration in the film, TS decreased dramatically. Addition of casein at concentrations as low as 10 wt % decreased the film TS significantly. This could be attributed to the higher protein content of casein. Above 30 wt % casein, the film TS decreased again. Since whey is comprised of approximately 70 wt % lactose, alginate/sodium lactate films were prepared containing various amounts of pure whey protein and lactose to examine the affect of lactose on the film TS. As shown in Figure 2c, increasing the amount of lactose relative to whey protein resulted in weaker films.

To prepare strong films with good barrier properties and maintain the hydrocolloid/plasticizer ratio at approximately 2.5, WVP measurements were carried out for films containing 50 wt % hydrocolloid, 30 wt % milk-based material, and 20 wt % plasticizer. As shown in Table 4, synthetic films have significantly lower WVP values than hydrocolloid/milk-based films due to the hydrophilic nature of the edible film. Films containing milk-based material have higher RH and lower WVP values than films without protein. There was, however, no significant difference in WVP values for films containing different milk-based material. Therefore, simulated whole milk (SWM) containing 3.5% butter fat was used as the protein source for the remainder of the study. Of the three different hydrocolloids tested, alginate films containing SWM had the lowest WVP values (Table 5). With respect to the three plasticizers, sorbitol films had the lowest WVP values followed by glycerine and then sodium lactate. Addition of SWM to the three hydrocolloid film blends effectively reduced WVP values for glycerine-plasticized films between 29 and 34%, lactate-plasticized films between 15 and 24%, and sorbitol-plasticized films between 2 and 10% (compare Tables 3 and 5). The most significant result of the

Table 6. Tensile Properties of Hydrocolloid/Simulated Whole Milk Films

film type[a]	TS[b] (dyn/cm²)	CV	ETB[b] (%)	CV	modulus[b] (dyn/cm²)	CV
alginate/Gly	2.49E + 08a	11.07	1.78c	10.67	2.00E + 10a	11.15
Mexpec/Gly	2.03E + 08ab	23.79	4.91bc	57.35	0.95E + 10b	17.21
pectin/Gly	2.19E + 08ab	12.37	8.36b	33.42	0.90E + 10b	15.62
alginate/Lac	1.10E + 08b	4.97	>13a	1.34	0.34E + 10c	7.18
alginate/Sorb[c]						

[a] 50 wt % hydrocolloid/30 wt % SWM/20 wt % plasticizer. [b] Values followed by different letters are significantly different at $p < 0.05$ using the Bonferroni lsd multiple-comparison method. [c] Too brittle to test.

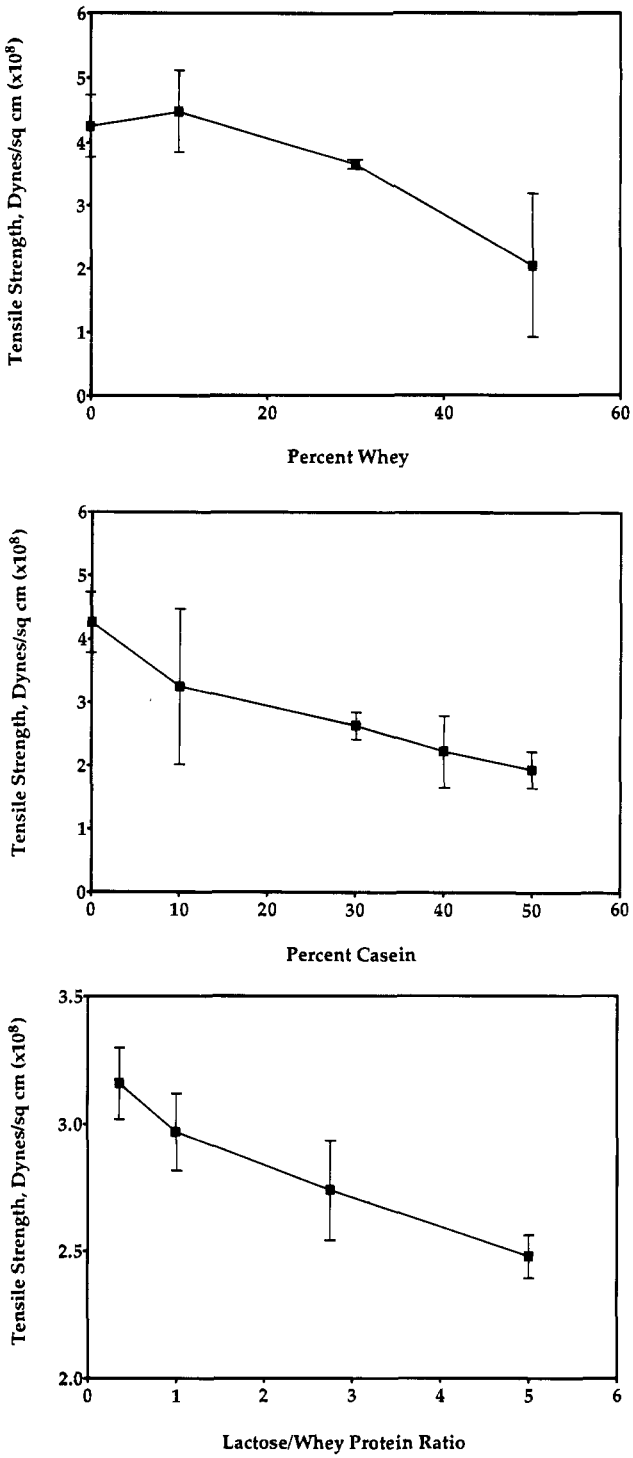

Figure 2. Effect of protein concentration on film tensile strength. Films contain 15 wt % sodium lactate and (a, top) 85 wt % (sodium alginate + whey), (b, middle) 85 wt % (sodium alginate + casein), or (c, bottom) 55 wt % sodium alginate + 30 wt % (whey protein + lactose).

tensile properties for films containing SWM (Table 6) was that the pectin/glycerine films were stronger and more flexible at a similar ratio of hydrocolloid to plasticizer (compare Tables 2 and 6). Alginate/sodium lactate films had ETB values greater than 13% and were less stiff at the same hydrocolloid to plasticizer ratio (compare Tables 1 and 6). Films containing sorbitol as the plasticizer were too brittle to test.

Future studies will be directed to improving tensile and water vapor barrier properties through thermal or ionic cross-linking of the milk protein polypeptide chains and covalent bonding of protein and hydrocolloid using traditional processing conditions.

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