Functional Properties of Edible Films Using Whey Protein Concentrate

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ABSTRACT

Methodologies were developed to form edible films of simple proteins or protein-lipid composites using whey protein concentrate. The functional properties of whey protein concentrate films were compared with those of the films derived from sodium caseinate, potassium caseinate, calcium caseinate, and whey protein isolate. Water vapor permeability of simple whey protein concentrate film was lower than that for films of sodium caseinate, potassium caseinate, and whey protein isolate. Composite whey protein concentrate film had the lowest water vapor permeability of all the milk protein films. The ultimate tensile strengths of simple whey protein concentrate films were similar to those of caseinate films. Whey protein concentrate films exhibited lower puncture strengths than did films from other milk proteins except simple film from sodium caseinate. Whey protein concentrate and isolate films had higher elongation values than did simple calcium caseinate films. Transmission electron microscopy revealed the presence of residual milk fat embedded in the protein matrix in whey protein concentrate films. Whey protein concentrate films had good water vapor barrier and mechanical properties that were comparable with those of films from other commercial milk proteins.

(**Key words**: edible films, whey protein concentrate)

Abbreviation key: **AM** = acetylated monoglyceride, **CC** = calcium caseinate, **EL** = elongation at break, **MC** = moisture content, **PC** = potassium caseinate, **PS** = puncture strength, **RH** = relative humidity, **SC** = sodium caseinate, **UTS** = ultimate tensile strength, **WPC** = whey protein concentrate, **WPI** = whey protein isolate, **WVP** = water vapor permeability.

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INTRODUCTION

It is estimated that 86 billion kg of whey are produced annually worldwide; the US dairy industry alone produces more than 18 billion kg of sweet cheese whey and 1.7 billion kg of acid whey, containing approximately 164 million kg of whey proteins (29). A report in 1989 (21) stated that 6.5 billion kg/yr of waste is produced because of whey disposal. More recent reports (1) indicate that only about 50% of the fluid whey produced in the US has been used for human food and animal feed applications from 1972 to 1992. The substantial amount of whey disposal in waste streams has caused environmental concerns, and the utilization of excess whey is necessary to reduce dairy waste. Manufacturing of edible films from whey protein products might represent an effective means of increasing utilization of excess whey and thereby alleviating the whey disposal problem.

Films are formed principally by cohesive forces between the polymer molecules and by adhesive forces between the film and the substrate (17). Cohesion and adhesion are related to the polymer structure and chemistry. Denaturing and crosslinking additives promote molecular order and, therefore, increase cohesion and rigidity of films (17). Under conditions of complete denaturation, whey protein chains are fully unfolded to a random coil conformation (7). For instance, at pH 6.5, irreversible denaturation of β-LG commences at 70°C (27). Irreversible thermal denaturation of β-LG occurs from aggregation involving sulfhydryl groups (27). The presence of lactose,

however, increases the minimum temperature required for thermal denaturation (5).

Whey protein fractions (α-LA and β-LG) and whey protein isolate (**WPI**; >90%) have been studied for film formation (23, 24, 26). Transglutaminase catalyzed crosslinking of the whey protein fractions (23), and thermal denaturation of WPI solutions (24) was used to facilitate film formation. Use of pure whey protein sources and enzymatic approaches can be rather expensive for commercial film making. Whey protein concentrates (**WPC**), however, are abundant in the US and are more readily available, thus making it worthwhile to explore their potential as edible film.

The water vapor barrier properties of a variety of caseinates and WPI films have been evaluated (22, 24). Those investigations were conducted mainly to study the effect of various plasticizers and lipids on the water vapor permeability (**WVP**) of the milk protein films. The effects of pH adjustment, calcium crosslinking, and lipid contents on the WVP of caseinate-based films have also been investigated (4). Large quantities of lipids, such as acetylated monoglyceride (**AM**) and beeswax, were added to the film formulations to reduce WVP. However, lipid addition at high rates might adversely affect the mechanical strength and structural integrity of these films. No study has been reported in the literature so far on the WVP of films from WPC.

Most foods undergo stress during storage, handling, and distribution. Edible films and coatings that are intended for food applications must therefore possess good mechanical properties. Ultimate tensile strength (**UTS**) is one of the important mechanical properties for packaging films. The UTS of films from corn zein, wheat protein, and soy proteins have been extensively reviewed (6, 15). The tensile properties of WPI films have been determined (26). The effect of adding beeswax to the WPI solution on the tensile properties was not quantified. The puncture strengths (**PS**) of films formed from whey protein fractions (α-LA and β-LG), facilitated by transglutaminase crosslinking, have been measured using a simple device (23). No information was given on the tensile properties of these films. The standard methods for testing UTS of thin films (3) require that all films be conditioned 23 ± 2°C and 50 ± 5% relative humidity (**RH**) for not less than 40 h, but most of those investigations did not condition films before tensile testing.

An Instron universal testing instrument (Instron Corporation, Canton, MA) was generally used to determine the tensile properties of edible films. The specimen size was fairly large and therefore subject to greater variation in thickness across the sample. Previous studies (9, 10) reported the use of a universal biomaterial tester for studying the UTS and PS of casein, wheat gluten, and methylcellulose films and found those measurements to be precise and repeatable. A stress concentrator was introduced at a small film strip to ensure the location of the breaking point of the film, resulting in a truly representative measurement of tensile profile and avoiding errors from breakage at random weak spots. Prior to the studies conducted in this laboratory, information was limited on mechanical properties of the films based on caseinates and WPC.

The specific objectives of this investigation were 1) to develop methodologies for forming simple protein and composite protein-lipid films based on WPC, 2) to study the moisture barrier and mechanical properties of the films, and 3) to compare protein films to other milk protein films.

MATERIALS AND METHODS

Materials

The materials used for film-forming solutions were sodium caseinate (**SC**; Alanate 191, 90.7% protein), calcium caseinate (**CC**; Alanate 391, 89.9% protein), potassium caseinate (**PC**; Alanate 351, 89.5% protein; New Zealand Milk Products Co., Inc., Santa Rosa, CA), WPI (BiPro, 93.6% protein; Davisco International, Inc., Le Seur, MN), WPC (76.6% protein; Vermont Whey Co., Inc., St. Albans, VT), glycerine (OPTIM, >99%; Dow Chemical Co., Inc., Midland, MI), and AM (Eastman Kodak Co., Inc., Rochester, NY).

Methods

Film Formation. A complete 2 × 5 experiment was designed for film making. The experiment consisted of two types of aqueous systems, simple protein solution and composite protein-lipid solution, and the five protein products. One batch of films was made for each of the 10 formulations.

The simple protein solutions (10%, wt/wt) were prepared using the method recommended for laboratory preparation of high solid casein and caseinate dispersions (32). Caseinates and whey protein products do not always go into solution readily, but this method allowed a quick and uniform dispersion in water. A measured quantity (adjusted to percentage of total solids) of a protein product was added into an ice-water (1:1; wt/wt) mixture that had been previously processed on the grind setting for 1 s in a blender (model 554CK; Hamilton Beach, Washington, NC). The protein and ice-water mixture was ground for 15 s. The solution was manually mixed for 30 s and then blended for an additional 15 s. The solutions were then mechanically stirred for 8 min to form uniform solutions using an electric motor-driven propeller.

Various temperatures and pH conditions were tested for a reproducible and reliable film-forming condition to denature the proteins in WPC. At pH less than 6.5, proteins precipitated or coagulated. The conditions of 75°C for 30 min after the solution pH adjusted to 6.6 using 2 *M* NaOH were identified to produce the solutions that ensured uniform film production. The solution was homogenous and without flocculating or precipitating particles. The WPI solutions were denatured at 90°C for 30 min without adjustment for pH according to the method in the literature (24). The denatured whey protein solutions were cooled down to room temperature in a water bath. Glycerine was added to all protein solutions at 1:2 (wt/wt; glycerine:protein) as a plasticizer.

The protein-lipid composite solutions were formed by reheating the prepared simple protein solutions to 60°C, adding AM at 1:2 (wt/wt, lipid:protein), and then blending for 3 min. All the simple protein solutions and protein-lipid composite solutions were degassed using a laboratory vacuum until no air bubbles were observed.

Film Casting. Film-forming solutions were cast on disposable polystyrene Petri dishes (VWR Scientific, Greenbelt, MD) of 9.1-cm diameter. The total solids content on each plate was maintained at 1.2 g to minimize thickness variations. Cast solutions were allowed to dry for 18 h at 23 ± 3°C. Dried films were peeled intact from the Petri dishes.

Film Conditioning. All films were conditioned in a walk-in environmental room (model 11-13RL; ENVIRONAIR System, East Longmeadow, MA) at 23 ± 2°C and 55 ± 3% RH for at least 48 h prior to tests.

Gel Electrophoresis. To characterize qualitatively the protein fractions of commercially produced WPC, WPI, and SC, SDS-PAGE was conducted (18). The stacking gel and separating gel contained 3.25% and 12.9% of polyacrylamide, respectively (ratios of acrylamide to bisacrylamide, 15:1 in both).

Thickness of Films. A micrometer (293-766; Mitutoyo, Tokyo, Japan) was used to measure the dry film thickness to the nearest .001 mm before all tests. For WVP and puncture tests, a mean was calculated from 10 measurements made randomly across each piece of film. For tensile tests, a mean of five measurements across each cut specimen was used.

Moisture Content. The moisture contents (MC) of the films were determined gravimetrically in triple determinations by drying samples at 100°C in a forced-air oven (model 1330-F; VWR, Bridgeport, NJ) for 48 h.

WVP. A modified WVP method of ASTM (American Society for Testing and Materials) was adopted (3, 25). Distilled, deionized water (20 ml) was filled in a circular test cup with an inside diameter of 6.3 cm. The corrected RH immediately under the film was noted. The mean gap between the water level in the cup and the film sample ranged between 9 and 10 mm after the test, depending on the WVP of the film. McHugh et al. (25) have recommended that the mean gap after the test must be less than 14 mm. A fan blowing across the surface of the test cups was used to supplement air circulation in the chamber to ensure equilibrium in the partial pressure of the water vapor. The test was conducted in the environmental chamber at 23 ± 2°C and 55 ± 3% RH for 24 h. The WVP tests were conducted using three sheets of each film type, and the results were reported as the mean value of the triple determinations in gram·millimeters per squared meter per hour per kilopascal.

Mechanical Properties. Mechanical strengths of the films were evaluated by tensile and puncture tests using a miniature universal tester (Vitrodyne® V-1000; Liveco, Burlington, VT) in the environmental chamber at 23 ± 2°C and 55 ± 3% RH (11).

Tensile Test. A uniform film specimen of 40 × 5.5 mm was prepared using a custom-made cutting tool, consisting of a pair of paral-

lel razor blades. A stress concentrator section ("dumbbell") was introduced in the middle of the sample by cutting two sectional circles opposite to each other. The width of the stress concentrator was noted to calculate the cross-sectional area. Film was loaded on the grips and clamped tightly, and the initial gauge length was noted. A tensile motion of 5 mm/s was then initiated. The force-displacement curve was recorded. The instrumental control and data acquisition were performed using a personal computer (model 316SX; Dell Computer Corporation, Austin, TX). The UTS was defined as the peak force divided by the cross-sectional area at the stress concentrator of specimen, and the value was reported in megapascals as the mean of triple determinations for each film type.

Elongation at break (EL) was the ratio between the displacement and the gauge length from the tensile curve of the same sample. The EL value was reported in percentage as the mean of triple determinations.

Puncture Test. A square sample of 24 × 24 mm was cut and placed between a specially designed film holder. The holder consisted of two plexiglass plates with four holes of 6.3-mm diameter each. Plates were held tightly by two screws. The puncture head was a cylindrical rod of 1.012-mm diameter, and puncture speed was set at 1 mm/s. The PS was measured in quadruple determinations and reported in megapascals; PS was defined as the peak force divided by the cross-sectional area of the probe.

Transmission Electron Microscopy. Small pieces of film were fixed in 2% osmium tetroxide vapors for 2 h. Films were then passed through a series of ethanol dehydration steps (once at 50% for 15 min, once at 75% for 15 min, and three times at 100% for 15 min each). The dehydrated films were immersed in propylene oxide and epoxy resin mixture (50:50, wt/wt) overnight and then transferred to 100% resin twice at intervals of 3 h each. Films were then embedded flat in epoxy resin and polymerized at 25°C in a UV chamber (Lica, Inc., Deerfield, IL). Ultrathin sections were cut using a Reichert Jung Ultracut E ultramicrotome (Lica, Inc.). Sections were mounted on copper grids. Microstructure was observed at 60 kV at different magnifications using a JOEL JEM-100CX II transmission electron microscope (JOEL USA, Peabody, MA).

Statistical Analysis. Analysis of variance and a multiple comparison procedure (Fisher's protected least significant difference) were applied to the data of film thickness, MC, WVP, UTS, EL, and PS to test for significance ($P \leq .05$) of effects of proteins, and film-forming liquid types. SuperANOVA™ (Abacus Concepts, Berkeley, CA) was used for all statistical tests.

RESULTS AND DISCUSSION

Composition

The manufacturers' data on the composition of the different milk protein products used in this study are listed in Table 1. The WPC had 76.6% protein, which was lower than that of all the other milk protein products used. The WPC also had 6.8% milk fat. Approximately 9% carbohydrates were present in the WPC as lactose-hydrolyzed products. The relative impurity in the WPC had some practical implications on the properties of the WPC films compared with those of the other films based on milk proteins, which are discussed in more detail in the following sections.

Gel Electrophoresis

Compositions of commercial milk protein products are subject to variation because of differences in processing methods and conditions, milk composition, and other factors (28). For commercial whey protein products, large variations in composition are also due to differences in cheese-making processes (28). It is therefore necessary to examine the characteristics of the commercial milk protein products. Three products (SC, WPC, and WPI) were characterized by SDS-PAGE. The qualitative differences in the products are shown in Figure 1. The SC sample contained α_s-, β-, and κ-caseins and some lower molecular weight proteins or peptides below the κ-casein zone.

The WPC and the WPI samples showed three well-defined protein bands of α-LA, β-LG, and BSA. In addition, the results of the electrophoresis suggested some additional protein bands between β-LG and BSA for the WPC and WPI products. Previous study (28) indicated that the whey protein products, especially WPC, varied greatly in the amounts of

TABLE 1. Composition[1] of the various milk protein products used in edible film formation.

Composition	SC[2]	CC	PC	WPI	WPC
	(%)				
Protein	90.7	89.9	89.5	93.6	76.6
Fat	1.2	1.4	1.1	. . .	6.8
Lactose	.5	.4	.1	. . .	.3
Carbohydrate	. . .	. . .	. . .	. . .	8.9
Ash	3.6	3.8	4.6	1.5	3.2
Moisture	4.0	4.0	4.4	4.3	4.6
pH	6.7	7.0	6.7	7.3	6.3

[1]Reported values are manufacturers' data.

[2]SC = Sodium caseinate, CC = calcium caseinate, PC = potassium caseinate, WPI = whey protein isolate, and WPC = whey protein concentrate.

proteins in this relatively undefined zone, and that this variation may affect functional characteristics of the product. The properties of the WPC films that were determined in this study were the characteristics of this particular product. The methods of film preparation might vary with compositional differences. The SDS-PAGE data, therefore, served as an index for product type. We suggest that the characteristics of milk protein products, as well as the quantitative data of the protein species, be reported in future studies of milk protein films, especially for those subject to large compositional variations.

Thickness

The thicknesses of all the simple and composite films are in Table 2. The mean thick-

TABLE 2. Water vapor permeability (WVP) of the simple and composite milk protein films.[1]

Film type	Thickness	MC[2]	WVP[3]	Corrected RH[4]
	(mm)	(%)	(g·mm/m^2·h·kPa)	(%)
Simple				
SC[5]	.109^{c}	20.92^{abc}	12.90^{a}	72.01
CC	.105^{c}	14.09^{d}	7.91^{c}	77.00
PC	.105^{c}	23.48^{ab}	12.57^{a}	71.88
WPC	.110^{bc}	20.18^{bc}	10.64^{b}	74.30
WPI	.111^{bc}	25.14^{a}	12.12^{a}	72.81
Composite				
SC	.141^{a}	17.38^{cd}	11.63^{ab}	75.98
CC	.156^{a}	24.92^{a}	7.46^{c}	82.00
PC	.153^{a}	16.80^{cd}	8.12^{c}	75.23
WPC	.116^{bc}	24.31^{ab}	3.95^{d}	85.56
WPI	.124^{b}	20.60^{abc}	11.80^{ab}	74.37
SE	.005	1.55	.49	.61
df	20	20	20	20

[a,b,c,d]Means in the same column without a common superscript differ ($P < .05$).

[1]All tests were carried out in an environmental chamber at 23 ± 2°C and 55 ± 3% relative humidity (RH).

[2]Moisture content.

[3]As means of triplicate determinations.

[4]Corrected RH on underside of film as means of triple determinations (25).

[5]SC = Sodium caseinate, CC = calcium caseinate, PC = potassium caseinate, WPC = whey protein concentrate, and WPI = whey protein isolate.

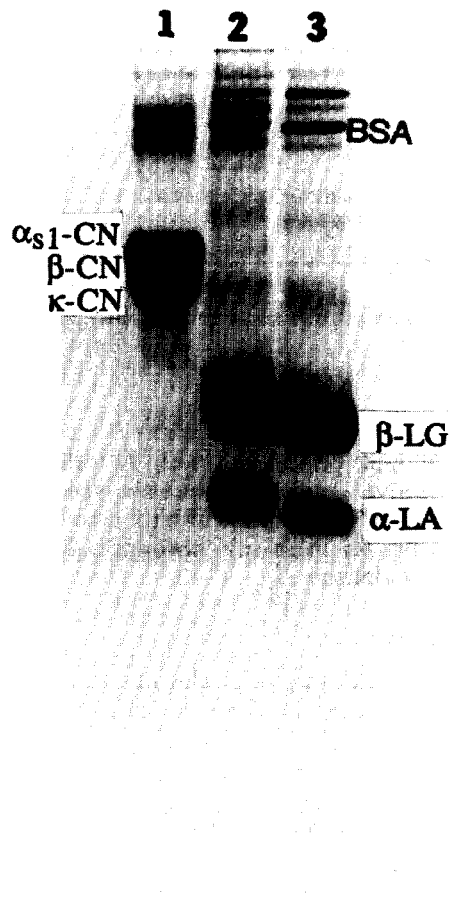

Figure 1. The SDS-PAGE patterns of proteins of 1) sodium caseinate, 2) whey protein isolate, and 3) whey protein concentrate.

nesses of composite caseinate films were significantly greater than those of the simple caseinate films ($P < .0001$) because of lower density of the lipid. There was no significant difference in the thickness among the simple protein films, among the composite caseinate films, and between two composite whey protein films ($P > .05$). The composite whey protein films were thinner than the composite caseinate films ($P < .05$).

The standard deviation of the film thickness ranged from .001 to .003 mm and .002 to .009 mm for of the simple protein films and the composite films, respectively. The method of constant total solids per plate resulted in films with uniform thickness, which was prerequisite for a precise determination and comparison of the mechanical and water vapor barrier properties of thin films.

MC

The MC of the edible films are shown in Table 2. The mean MC of simple protein films (21.8%) was slightly higher than that of the composite films (20.5%). Addition of lipid to the film-forming solutions made the films more hydrophobic; therefore, the composite films should contain less moisture than the simple protein films. This statement was supported by the data of the SC, PC, and WPI, but not of the CC and WPC films. Variation in the MC determination (mean coefficient of variation = 12%) was relatively large. A sample size of 6 is recommended for the determination if the same procedure is used (14).

Among simple protein films, CC film had a significantly lower MC than others ($P < .05$). It was suggested that ionic crosslinking in the simple CC film reduced protein polymer segmental mobility (4), resulting in lower MC. Composite whey protein films had higher mean MC than did the caseinates ($P < .05$). The PC films had the lowest MC in the composite group.

In the study of milk protein gels, proteins with high amounts of apolar residues, such as Val, Pro, Leu, Ile, Phe, and Trp, formed coagulum-type gels with low water-holding capacities; those with low amounts of these apolar residues formed translucent gels with high water-holding capacities (13). Proteins containing greater than 31.5% of these nonpolar residues formed coagulum-type gels, and those with less than 31.5% nonpolar residues formed translucent gels (31). Commercial caseinate, on average, contains 37.9% of the nonpolar residues per mole of protein, and commercial WPI, 29.6% (15). A similar trend in the water-holding capacity of milk protein gels was observed for SC and WPI films when the latter contained more water than the SC films. Although most water in a protein gel is held by water entrapment and immobilization in the protein network or matrix (20), in a protein film, water is held by H bonding, ion hydration, and hydrophobic interaction; the concentration of apolar groups appears to have a

similar effect on product MC. Other factors, such as protein conformation, amino acid sequences, distribution of hydrophilic and hydrophobic groups, the extent of protein unfolding, polarity, pH, ionic strength, and environmental conditions, affect the water-binding capacities of food proteins (13, 30). To understand these effects fully, future research must study water sorption by films at different humidity conditions.

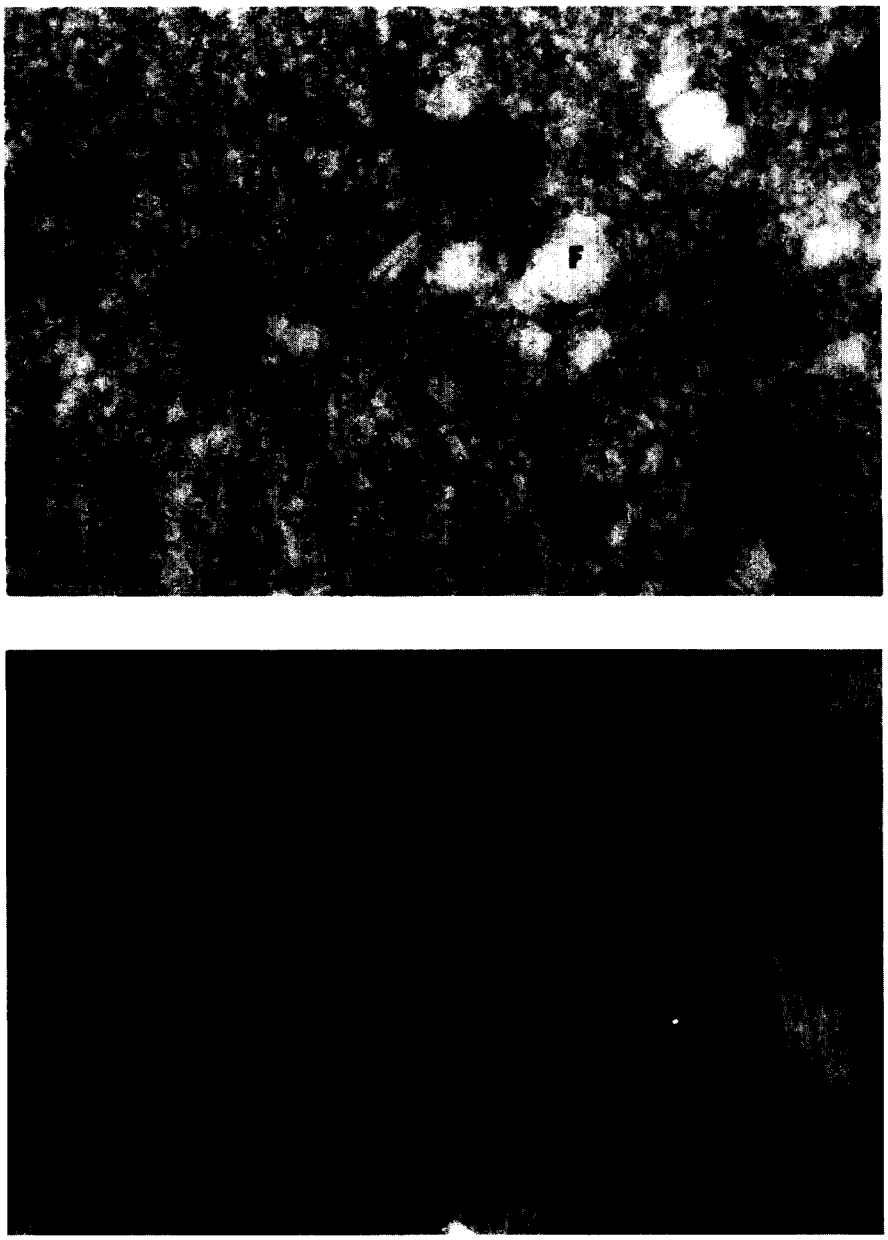

Figure 2. Transmission electron micrographs of simple whey protein concentrate film containing milk fat (top) and a simple whey protein isolate film (bottom). F = Milk fat; P = whey protein matrix. 60 kV. ×43,000. Scale bar = .8 μm.

WVP

The mean WVP of the milk protein films are listed in Table 2. The simple WPC film had a mean WVP of 10.64 g·mm/m^2·h·kPa, which was significantly lower than that of WPI ($P < .05$), PC, and SC films ($P < .0001$). The WPC product used had a residual fat content of 6.8%. A transmission electron micrograph of a simple WPC film (Figure 2, top half) revealed the presence of milk fat and other minor constituents that were embedded in the whey protein matrix. The presence of residual milk fat (about .6% of the solution) could play a role in imparting lower WVP to its films.

The simple CC film tested had the lowest WVP (7.9 g·mm/m^2·h·kPa) among all simple milk protein films ($P < .001$). Ionic calcium (Ca^{2+}) is known to form strong molecular crosslinking in films based on caseinates (4). Strong ionic crosslinking reduced segmental mobility of the protein polymer in the CC films (4), consequently making them less permeable to water vapor than other films based on milk proteins.

The WVP properties of casein and caseinate films increased in the following order: magnesium caseinate, CC, micellar casein, SC, PC, and rennet casein in other work (19). A similar trend was observed during this investigation; the WVP of the various milk protein films increased in the following order: CC, WPC, WPI, PC, and SC. The difference in the WVP of PC and SC films was not significant ($P > .05$).

For composite films, WPC films had a WVP of 3.95 g·mm/m^2·h·kPa, which was significantly lower than those for all caseinate and WPI films. Addition of AM to the WPC film-forming solution, which already contained residual milk fat, increased the hydrophobicity of the film and rendered it the least permeable to water vapor among the milk protein films tested. The result was similar to that from addition of butter oil plus AM to SC solution, which resulted in films with lower WVP than those with either AM or butter oil (11). The data suggest that the presence of milk fat in the film system indeed contributed to lowering the WVP of the WPC film.

The milk protein films tested in this study had much higher WVP values than did synthetic films. At 23 ± 2°C and 55 ± 3% RH, low density polyethylene (LDPE) film with thickness of .014 mm had a mean WVP of .002 g·mm/m^2·h·kPa, and Saran® (DowBrands L.P., Indianapolis, IN) with a mean thickness of .012

TABLE 3. Ultimate tensile strengths (UTS), elongations at break (EL), and puncture strengths (PS) of simple and composite milk protein films.[1]

Film type	A[2]	UTS	EL	PS
	(mm^2)	(MPa)	(%)	(MPa)
Simple				
SC[3]	.292	2.98^{cd}	29.89^{b}	1.92^{cd}
CC	.285	4.25^{b}	1.45^{g}	5.44^{a}
PC	.308	2.97^{cd}	42.80^{a}	2.03^{c}
WPC	.224	3.36^{bc}	20.84^{cd}	1.69^{d}
WPI	.269	5.94^{a}	22.74^{cd}	2.80^{b}
Composite				
SC	.410	1.32^{ef}	27.42^{b}	.84^{e}
CC	.352	2.14^{de}	13.40^{ef}	.79^{e}
PC	.330	1.55^{ef}	17.74^{de}	.72^{e}
WPC	.349	1.08^{f}	13.58^{ef}	.26^{f}
WPI	.242	3.15^{c}	10.78^{f}	2.07^{c}
SE	.045	.36	2.10	.09
df	20	20	20	30

[a,b,c,d,e,f,g]Means in the same column without a common superscript differ ($P < .05$).

[1]All tests were carried out in an environmental chamber at 23 ± 2°C and 55 ± 3% relative humidity.

[2]Cross-section area of stress concentrator.

[3]SC = Sodium caseinate, CC = calcium caseinate, PC = potassium caseinate, WPC = whey protein concentrate, and WPI = whey protein isolate.

mm had WVP of .00016 g·mm/m^2·h·kPa (8). Straight-chain polymers in synthetic films resulted in a higher degree of molecular order and low permeabilities. Milk protein films, however, are hydrophilic in nature and therefore had higher permeabilities. The Ca^{2+} crosslinking and alteration of pH of film-forming solutions reduce WVP (4).

UTS

The UTS of the simple and composite milk protein films are listed in Table 3. Simple milk protein films had significantly higher UTS than their composite counterparts ($P < .001$). Addition of lipid weakened edible films. Lipid concentration of composite SC film was linearly and inversely related to UTS (12). Therefore, composite film formulations should be carefully considered because excessive lipid might result in films with very poor mechanical properties.

Simple WPI film had UTS that was significantly higher ($P < .0001$) than those of all the caseinates and WPC films. The UTS of simple WPC film was higher than those of SC and PC films. The Ca^{2+} crosslinking made CC film significantly stronger than the other caseinates ($P < .001$). The UTS of CC film was 22% higher than that of WPC film. Composite WPC films had UTS values that were comparable with those of SC and PC films but significantly lower than those of WPI and CC films ($P < .0001$). The WPI film had the highest UTS in the composite group of films as well.

The WPI had the highest protein concentration and was a highly purified protein product (Table 1). There was less interruption between proteins by small molecules. Also, thermal denaturation promotes covalent interaction between proteins by random disulfide bonding, resulting in a rigid protein matrix. A smooth surface of a tight protein matrix in the WPI film was revealed in the transmission electron micrographic study (Figure 2, bottom half). Consequently, WPI films exhibited the highest UTS. The WPC product, however, with lower protein concentrations and greater impurities, such as milk fat and carbohydrates, resulted in a weaker film. A study on the gel strengths of various WPI and WPC products (28) showed that the true shear stress of WPI gels of 10% protein concentration was generally much greater than that of WPC gels of the same concentration. A similar relationship was observed from our data on film strength. Nevertheless, the WPC films with covalent bonding between proteins still had higher UTS than those of SC and PC films.

The UTS of synthetic films, the low density polyethylene and Saran®, were determined to be 31 and 69 MPa, respectively, using the same method (8). These synthetic films were almost 10 times stronger than the milk protein films equilibrated at 55% RH. The milk protein films had UTS that were comparable with wheat and soy protein films (6, 16). Cellulose film exhibited considerably higher UTS (16). Cellulose and other synthetic polymers generally consist of long straight chains that impart greater molecular order, thereby resulting in strong and rigid films.

EL

Table 3 shows the elongation properties of the milk protein films. The simple protein films generally had higher EL values than the composite protein films. Simple PC film was the most stretchable film among the films tested. The simple CC film was extremely brittle; addition of lipid improved its EL. Importantly, the MC of the composite CC film was significantly higher than the simple CC film ($P < .01$). Simple and composite SC films had similar EL values. Also, their MC were not significantly different ($P > .05$). Whey protein films (WPI and WPC) had EL values in the range of 20 to 25%, which were not significantly different from each other ($P > .05$) within their solution types. Their MC were also similar.

PS

Table 3 lists the PS of the various milk protein films. Simple protein films exhibited significantly higher PS than did composite films ($P < .0001$). The PS of the simple film-forming materials increased in the following order: WPC, SC, PC, WPI, and CC. The WPC films had lower PS than the films from other milk protein sources partially because of the weakening by impurity and lubrication caused by residual milk fat in the films. Furthermore, the low protein concentration of WPC resulted in films with less resistance to puncture. Sim-

ple CC film had the highest PS in addition to the second highest UTS (Table 3).

For composite films, the addition of lipid significantly reduced the PS because of the expected weakening and lubricating effects of lipid on the milk protein films. Similar to the simple protein films, the composite WPC films had the lowest PS. Composite WPI film exhibited the highest PS, which may be due to its high protein concentration and high purity of the product primarily. All of the composite caseinate films had similar PS.

Relationships between MC and Film Performances

The coefficients of determination of linear regressions of the equilibrium MC of the caseinate films and their functional properties fell between .901 to .998 ($P < .05$) (Figure 3). The caseinate films with higher MC had higher WVP and EL. An inverse relationship was observed between the MC of the caseinate films and their UTS and PS. Although three different films were compared, results may suggest possible impacts of MC on the film performances. More conclusive investigation should be conducted for the films of common protein products over a wide range of humidity and temperature. The information will be useful in predicting the storage stability and performance of the films.

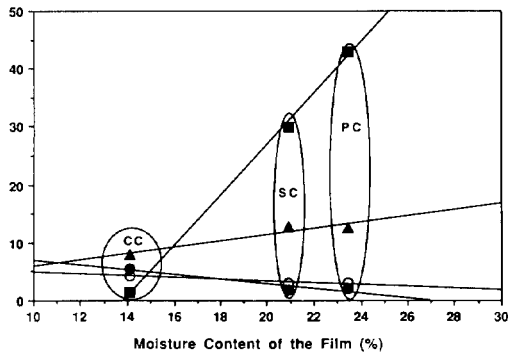

Figure 3. Relationship of moisture content to the elongation (■, %), ultimate tensile strength (O), MPa), puncture strength (●, MPa), and water vapor permeability [▲ g·mm/(m²·h·kPa)] of simple caseinate films (CC = calcium caseinate, SC = sodium caseinate, and PC = potassium caseinate).

CONCLUSIONS

The WPC was used to form smooth and flexible films, which served as better moisture barriers than WPI and some of the caseinate films. The WPC films exhibited higher UTS than did some of the caseinates. The stretchability of WPC films was similar to that of WPI films. Whey protein products with higher purity, such as WPI, produced stronger films. The results with simple caseinate films suggested that a relationship might exist between the functional behaviors and the equilibrium MC of films based on caseinates. The WPC film appears to be more attractive than WPI for food applications because of the comparable functional performance and relatively less expensive material. Utilization of the excess whey in the form of WPC could effectively alleviate the whey disposal problem by their conversion into value-added products, such as edible films and coatings.

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