ENGINEERING/PROCESSING

Mechanical and Barrier Properties of Lactic Acid and Rennet Precipitated Casein-Based Edible Films

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ABSTRACT

Tensile strength (TS), percent elongation (%E), oxygen permeability (OP), and water vapor permeability (WVP) of lactic acid and rennet precipitated casein-based edible films were studied to determine the effect of protein to plasticizer ratio (0.6:1, 1:1, 1.4:1) and plasticizer type (sorbitol, glycerol) on these properties. TS increased (p<0.05) with increase in protein to plasticizer ratio. Sorbitol plasticized films were stronger (p<0.05) than glycerol plasticized films. However, films plasticized with glycerol were more extensible (p<0.05). Film %E decreased with increase in protein/plasticizer ratio for lactic acid casein films, whereas it increased for rennet casein films. Films plasticized with sorbitol were more effective (p<0.05) moisture and oxygen barriers than glycerol plasticized films. Overall, lactic acid casein films plasticized with sorbitol had the most effective mechanical and barrier properties.

Key Words: lactic acid, rennet, casein, edible films

INTRODUCTION

EDIBLE FILMS SUCH AS SAUSAGE CASINGS, WAX COATINGS, GELatin capsules, sugar and chocolate have been used in food applications for many years (Guilbert, 1986). Interest in edible films and biodegradable polymers has been renewed due to concerns about the environment and a need to reduce the amount of disposable packaging as well as demands by consumers for higher quality food products. Edible films can function as secondary packaging materials to enhance food quality and reduce the amount of traditional packaging material required. For example, by acting as moisture and gas barriers, edible films can enhance food quality and may provide protection for a food product after the primary packaging is opened. Their purpose is not solely to replace synthetic polymers or provide biodegradable counterparts but they provide opportunities for new product development as well (Krochta and DeMulder-Johnston, 1997).

McHugh and Krochta (1994a) reviewed milk protein-based edible films and coatings. When non fat dry milk (NFDM) was investigated as the starting material for edible film production, lactose crystallization interfered with the film forming process (Maynes and Krochta, 1994). Earlier studies with caseins and whey protein films involved enzymatic crosslinking of proteins using transglutaminase (Motoki et al., 1987a, b; Mahmoud and Savello, 1992, 1993). Ho (1992) reported on the water vapor permeability of caseinate (magnesium, calcium, sodium and potassium caseinate) films as well as micellar and rennet casein films produced without crosslinking enzymes. Effect of incorporating lipids on the water vapor permeability (WVP) of such films was reported by Ho (1992). Avena-Bustillos and Krochta (1993) investigated the effects of pH adjustment, calcium cross-linkage and lipid content on the WVP of caseinatebased edible films. By monitoring heat, pH and protein concentra-

Authors Chick and Ustunol are with the Dept. of food Science & human Nutrition, 2105 S. Anthony Hall, E. Lansing, MI 48824. Address inquiries to Dr. Z. Ustunol. tion McHugh et al. (1994) produced films from whey protein isolate without cross-linking enzymes. The effect of incorporating lipids to reduce the WVP of whey protein isolate edible films has also been reported (McHugh and Krochta, 1994d).

Lactic acid and rennet precipitated caseins have not been studied as extensively for film formation. Random coil nature of caseins, their ability to hydrogen bond and interact electrostatically make both of these caseins useful for edible film production. Their emulsifying ability also makes them suitable for production of emulsion films. Both lactic acid casein and rennet casein have been used in production of plastics. Properties of rennet plastics are more effective than those of acid caseins (Southward, 1989). Acid and rennet caseins have been used for paper and paperboard coatings (Southward, 1989). We hypothesize that properties of both lactic acid and rennet precipitated caseins should make them very effective for the production of edible films. Our objective was to develop edible films from lactic acid and rennet precipitated casein and determine the effect of protein/plasticizer ratio and plasticizer type on film barrier and mechanical properties.

MATERIALS & METHODS

Materials

Lactic acid casein (Alacid 710, 30 mesh) and rennet casein (Alaren 771, 30 mesh) were obtained from New Zealand Milk Products (North America) Inc., (Santa Rosa, CA) (Table 1). Glycerol was obtained from Mallinckrodt Speciality Chemicals Co. (Paris, KY). All other chemicals were purchased from Sigma (St. Louis, MO).

Film preparation

Lactic acid or rennet casein (3, 5 or 7% w/w) and sorbitol or glycerol (5% w/w) were mixed in distilled water and the pH adjusted to 10 with 1M NaOH. Solutions were heated to $65.6 \pm 1.0^{\circ}$ C for 45 min while being stirred continuously. Samples were filtered through a layer of cheesecloth and held at room temperature (~23°C) for 4h to allow the foam to settle. The solutions were vacuum degassed for 30 min and then cast on an 18 cm circular teflon surface. The films were dried in a gravity convection oven (Blue M Electric Co., Blue Island, IL) at 55°C until constant weight was reached. The dried films were peeled, wrapped in aluminum foil and stored at room temperature (~23°C) until tested.

Table 1-Composition and pH of caseins for film preparation^a

Components	Lactic acid casein	Rennet casein
Protein (N x 6.38) %	87.3	80.6
Ash %	1.8	7.8
Moisture %	9.6	11.0
Fat %	1.2	0.5
Lactose %	0.1	0.1
pH⁵	4.6	7.1

^aData provided by New Zealand Milk Products (N. America) Inc. ^b5% at 20°C Table 2-Effect of protein to plasticizer ratio and plasticizer type on tensile strength of lactic acid and rennet precipitated caseinbased edible films (23°C, 50% RH)

		Мр	a	
Casein: plasticizer	Lactic ac	id casein	Rennet	casein
ratio	Sorbitol	Glycerol	Sorbitol	Glycerol
0.6:1	2.43ª	0.42 ^d	3.83ª	0.83 ^d
	(0.08)	(0.06)	(0.31)	(0.29)
1:1	7.48 ^b	1.24°	9.53 ^b	2.42°
	(0.75)	(0.03)	(1.41)	(0.17)
1.4:1	11.65°	2.51	15.12°	4.50 ^f
	(0.38)	(0.07)	(2.27)	(0.70)

a-fMeans with standard deviations in parentheses. Means with the same superscript are not significantly different (P<0.05). Comparisons are made within the same column and row for each case in type. Treatments were replicated three times, each test was conducted in duplicate.

Film thickness

Film thickness was determined using a TMI model 549M micrometer (Testing Machines Inc., Amityville, NY). For determining barrier properties, measurements were taken at five locations and the mean values were used for calculations. For mechanical properties three measurements were taken and averaged. The thickness of films used for barrier testing averaged 0.203 mm while thickness of films used for mechanical testing averaged 0.216 mm.

Mechanical properties

Film samples were cut into strips of 101.6 mm length and 25.4 mm width using a Precision Sample Cutter (Thawing Albert Instrument Co., Philadelphia, PA). Initial grip separation was 50.8 mm. All films were conditioned for 48h under the test conditions in a

controlled room prior to testing. Tensile strength (TS) and percent elongation at break (%E) were determined according to standard D882-91 (ASTM, 1992) using the Instron Universal Testing Machine Model 2401 (Canton, MA), at 23 2° C and 50 \pm 5% RH. A 1 kN static load cell and crosshead speed of 50.8 cm/min was used. Each treatment was tested in duplicate and all experiments were replicated three times.

Barrier properties

Oxygen permeability (OP). All film samples (50 cm2) were initially conditioned under the test conditions for 10h. Film OP was determined at 23°C and 0% RH according to method D3985-81 (ASTM, 1992) using an Oxtran 200 permeability tester (Modern Controls Inc., Minneapolis, MN). Temperature was maintained using an Endocal temperature control bath model RTE 100 (Neslab Instruments Inc., Newington, NH). Oxygen (21%) and air were used as test gases and nitrogen was the carrier gas.

Water vapor permeability (WVP). Sample size for all films was reduced from 50 cm2 to 5 cm2 with the use of aluminum foil backing. Samples were initially conditioned for 10h under the test conditions in a controlled room. WVP of the films was determined according to standard F1249-90 (ASTM, 1992) using the Permatran-W (Modern Controls Inc., Minneapolis, MN) at 37.8 ± 0.5 °C and 90 \pm 3% RH. A saturated potassium nitrate salt solution was used to obtain the desired RH. Polyester (0.025 mm thickness and water vapor transmission rate 21g H20/m2. d) was used as the reference film.

Statistical analysis

All experiments were replicated three times in a randomized complete block experiment. Days were blocked. Each film property was measured in duplicate. Statistical analysis was conducted using Sigma Stat 1.0 (Jandel Corp., San Rafael, CA). Treatment means were

Film type (protein:plasticizer)	Thickness (mm)	WVP (g.mm/m².d.kPa)	OP (cc.um/m²d.kPa)	TS⁵ (MPa)	E⁵ (%)	Reference
CZ-G (4.9:1)	0.10–0.33	7.69–11.49 (21°C, 85% RH)	13.0–44.9 (30°C, 0% RH)	(2)	(,	Park and Chinnan (1995)
SPI-G (1.7:1)	0.064		4.75 (25°C, 0% RH)	3.13–5.23	66.5-90.3	Brandenburg et al. (1993)
WG-G (2.5:1)	0.146		3.82 (23°C, 0% RH)			Gennadios et al. (1993a) &
	0.140	108.4 (26°C, 50%/100%RH)		1.8	25	Aydt et al. (1991)
NFDM-G lactose extracted (3.1:1)	0.069	81.0 (30°C, 61% RH)		5.1	12.2	Maynes and Krochta (1994)
NFDM-G ultra-filtered (3.1:1)	0.071	70.3 (30°C, 65% RH)		10.0	5.2	Maynes and Krochta (1994)
WPI-G (1.7:1)	0.121	119.8 (25°C, 65% RH)				McHugh et al. (1994)
WPI-S (1.7:1)	0.129	61.92 (25°C, 79% RH)				McHugh et al. (1994)
WPI-G (2.3:1)	0.110		76.1 (23°C, 50% RH)	13.9	30.8	McHugh and Krochta (1994c)
WPI-S (1:1)	0.110		8.3 (23°C, 50% RH)	14.7	8.7	McHugh and Krochta (1994c)
SC-G (2:1)	0.109	309.6 (23°C, 72% RH)		2.98	29.89	Banerjee and Chen (1995)
CC-G (2:1)	0.105	189.8 (23°C, 72% RH)		4.25	1.45	Banerjee and Chen (1995)
α _{s1} -casein -G (49:1)				4.1 (room temp)	38.0 (room temp)	Motoki et al. (1987a)
α_{s1} -casein -G transglutaminase				10.6 (room temp)	77.0 (room temp)	Motoki et al. (1987a)

aCZ=Corn zein. SPI =Sov protein isolate. WG=Wheat gluten. NFDM=Non-fat drv milk. WPI=Whey protein isolate. SC=Sodium caseinate. CC=Calcium caseinate. G=Glycerol. =Sorbitol, b Evaluated at 23°C and 50% RH, unless otherwise specified

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Table 4-Properties	; of	some	synthetic	polymers
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Table 4-Froperties	able + - Froperices of some synthetic polymers							
Polymer	Thickness (mm)	WVP⁵ (g.mm/m² d.kPa)	OP⁰ (cc µm/m²d.kPa)	TS⁰ (Mpa)	E° (%)	Reference		
LDPE	0.0254		1870	8.6-17	500	Salame (1986)		
HDPE	0.0254	0.02	427	17-35	300	Smith (1986)		
EVOH (56% VOH)	0.0254		0.066	39.2-68.7	235-325	Foster (1986)		
Nylon 6	0.0254	7.1	10.1	69-82.8	400-500	Tubrity and Sibilia (1986)		

^aLDPE=Low density polyethylene, HDPE=High densitry polyethylene, EVOH=Ethylene vinyl alcohol (VOH-Vinyl alcohol) ^bEvaluated at 37.8°C and 90% RH

cEvaluated at 23°C and 50% RH

compared using the Student-Newman-Keuls comparison. Comparisons were made only within the same case type. Significance of differences was defined at $p \le 0.05$.

RESULTS & DISCUSSION

COMPOSITION OF BOTH LACTIC ACID AND RENNET PRECIPITATED caseins were confirmed using AOAC (1990) procedures. Both lactic acid and rennet precipitated casein edible films plasticized with sorbitol and glycerol were odorless, clear, transparent and flexible.

Mechanical properties

Tensile strength (TS) the maximum tensile stress a film could sustain, is a measure of film strength, and for casein-based edible films increased (p<0.05) with increased protein and decreased plasticizer (Table 2). Decreases in TS with increases in plasticizer concentration have been reported in whey protein isolate films plasticized with sorbitol and glycerol (McHugh and Krochta, 1994c), in wheat gluten films plasticized with glycerol or polyethylene glycol (Park et al., 1994), in egg albumen films plasticized with sorbitol, glycerol or polyethylene glycol (Gennadios et al., 1996), and in chitosan films plasticized with glycerol (Butler et al., 1996). Films made with sorbitol had higher TS (p<0.05) than those made with glycerol. In glycerol plasticized films protein-protein interactions were probably reduced providing films with lower TS due to the more hydrophilic nature of glycerol (compared to sorbitol) giving it higher affinity to bind water at equivalent RH (Sicard and Leroy, 1983). Overall, films made with rennet casein had higher TS than lactic acid casein films (Table 2). We expected lactic acid casein films would be stronger than rennet casein films, since lactic acid casein was higher in total protein content (Table 1). However, this was not the case. Rennet casein was higher in ash content than lactic acid casein, which may have provided for additional electrostatic cross-linking between divalent cations and negatively charged groups along pro-

Table 5–Effect of protein to plasticizer ratio and plasticizer type on percent elongation (%E) of lactic acid and rennet precipitated casein-based edible films (23° C, 50% RH)

Casein: plasticizer ratio		9	6E	
	Lactic ad sorbitol	cid casein glycerol	Rennet sorbitol	casein glycerol
0.6:1	170.7ª	121.4 ^d	4.9ª	123.2 ^d
	(2.0)	(10.2	(0.8)	(22.4)
1:1	1`56.Ó⁵	253.6°	7.6 ⁶	185.4 [°]
	(6.1)	(16.3)	(1.5)	(22.8)
1.4:1	50.6°	194.1 ^ŕ	17.9 [°]	223.5 ^f
	(7.5)	(20.6)	(4.6)	(22.7)

^{a-f}Means with standard deviations in parentheses. Means with the same superscript are not significantly different (P<0.05). Comparisons are made within the same column and same row for each casein type. Treatments were replicated three times, each test was conducted in duplicate. tein chains and therefore formed stronger films (Table 3).

Our strongest film (rennet casein film plasticized with sorbitol) was stronger than soy protein isolate film plasticized with glycerol reported by Brandenburg et al. (1993), wheat gluten film plasticized with glycerol (Gennadios et al., 1993a), lactose extracted nonfat dry milk film plasticized with glycerol (Maynes and Krochta, 1994), or caseinate films plasticized with glycerol (Banerjee and Chen, 1995). They were comparable to whey protein isolate films plasticized both with glycerol and sorbitol (McHugh and Krochta, 1994c).

TS values of our films were comparable to those of a much thinner LDPE (Salame, 1986). Such comparisons (Table 4), however, may not be completely reliable since different films have varying compositions and were tested under different conditions (e.g. pretreatment, temperature, humidity, testing machine speed and film thickness). For our comparisons we selected films that were tested under the same temperature and RH conditions as our films.

Overall, glycerol plasticized films were more extensible (p<0.05)

Table	6-Effect	of protein	to plas	ticizer	ratio an	nd plasticiz	er type:
on ox	ygen perm	eability of l	actic aci	id and r	ennet p	recipitated	casein-
based	d edible fil	ms (23°C, (0% RH)				

Casein: plasticizer ratio	cc·µm/day⋅m²⋅kPa					
	Lactic ad	cid casein glycerol	Rennet sorbitol	casein glycerol		
0.6:1	0.65 ^a	0.88ª	0.71ª	7.06 ^b		
	(0.12)	(0.10)	(0.16)	(1.83)		
1:1	0.73ª	2.18 ^b	1.02ª	5.55 ^b		
	(0.13)	(0.54)	(0.27)	(2.84)		
1.4:1	0.81ª	0.73 ^a	0.96ª	1.84ª		
	(0.20)	(0.27)	(0.15)	(0.79)		

a-bMeans with standard deviations in parentheses. Means with the same superscript are not significantly different (P<0.05). Comparisons re made within the same column and same row for each casein type. n=3 for all treatments.

Table 7—Effect of protein to plasticizer ratio and plasticizer type on water vapor permeability of lactic acid and rennet precipitated casein-based edible films (37.8°C, 90% RH)

Treatments casein: plasticizer	g⋅mm/day⋅m²⋅kPa					
	Lactic ac Sorbitol	id casein Glycerol	Rennet Sorbitol	casein Glycerol		
0.6:1	44.9 ^{ab}	54.9ª	49.7 ^{ab}	57.9ª		
	(9.8)	(1,6)	(8.3)	(4.9)		
1:1	45.0 ^{ab}	59.3ª	49.6 ^{ab}	58.2 ^{ab}		
	(9.0)	(6.5)	(6.6)	(2.5)		
1.4:1	34.0 ⁶	54.7 ^a	39.6 ^b	45.2 ^{ab}		
	(5.2)	(6.2)	(3.6)	(6.8)		

^{a-b}Means with standard deviations in parentheses. Means with the same superscript are not significantly different (P<0.05). Comparisons are made within the same column and same row for each casein type. n = 3 for all treatments. than sorbitol plasticized films (Table 5). Glycerol being hydrophilic, binds water which further served as a plasticizer. In lactic acid casein films, %E decreased (p<0.05) with increase in protein content and decrease in plasticizer amount. Percent elongation of rennet casein films increased (p<0.05) with increase in protein content and decrease in plasticizer amount. This was contrary to reported results by Gennadios et al. (1994). They reported an increase in film elongation with decrease in protein and increase in plasticizer amount. Extensibility as determined by %E of our casein-based films was greater than most protein-based edible films and was comparable to those of soy protein isolate films plasticized with glycerol (Brandenburg et al., 1993) (Table 3).

Barrier properties

Overall, sorbitol films were better (p<0.05) oxygen barriers than glycerol films (Table 6). Increase in protein concentration and decrease in plasticizer amount did not affect film oxygen barrier properties except for rennet casein films plasticized with glycerol. The OP of films with 1.4:1 rennet casein to glycerol ratio was lower (p<0.05) than that of others. The higher ash content of rennet casein may have provided for cross-linking which, further reduced OP of these films. McHugh and Krochta (1994c) reported whey protein isolate films plasticized with sorbitol exhibited lower OP than glycerol films at several relative humidities. An exponential effect of relative humidity on OP has been reported in edible films (McHugh and Krochta, 1994c). We did not investigate the effect of relative humidity on oxygen barrier properties. Our casein-based edible films, being eight times thicker had comparable oxygen barrier properties to that of nylon and had better oxygen barrier properties than polyethylene (Table 4).

Polar polymers such as proteins, which associate by a high degree of hydrogen bonding, typically have low gas permeabilities, particularly at low RH (McHugh and Krochta, 1994b). However, a high degree of hydrogen bonding in a film does not necessarily provide for good moisture barrier properties. Because of the hydrophilic nature of proteins, our casein-based films similar to other proteinbased films were ineffective moisture barriers (Table 7). Overall, sorbitol plasticized films were more effective moisture barriers than glycerol plasticized films. McHugh et al. (1994) reported better moisture barrier properties in whey protein isolate films plasticized with sorbitol than those plasticized with glycerol. Similar to the OP data, increasing protein concentration or decrease in plasticizer amount had no effect (p>0.05) on film WVP. McHugh et al. (1994) reported an increase in protein concentration increased WVP of whey protein isolate films plasticized with sorbitol. In glycerol plasticized whey protein films, increasing glycerol concentration resulted in increased WVPs. In our casein films there were no notable effects due to protein/plasticizer ratio. Casein-based edible films were more effective moisture barriers than wheat gluten films plasticized with glycerol (Aydt, 1991), or whey protein isolate films plasticized with glycerol or sorbitol (McHugh et al., 1994). Our films were not as effective moisture barriers as sodium caseinate and calcium caseinate films plasticized with glycerol (Table 3).

CONCLUSIONS

BOTH LACTIC ACID AND RENNET PRECIPITATED CASEINS WERE suitable for production of edible films. Films produced from these two caseins had good mechanical and oxygen barrier properties, similar to other protein-based edible films but they were not very effective moisture barriers. Overall, lactic acid casein films plasticized

with sorbitol had the most effective mechanical and barrier properties.

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