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Production and Properties of Edible Film Using Whey Protein

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The utilization of excess whey is necessary to reduce dairy waste because the large amount of whey disposal in waste streams has caused environmental problems. During whey protein film production as the effective means of utilization of excess whey, we have examined the effects of pH, temperature, and plasticizers for water vapor permeability (WVP), tensile strength (TS), and elongation rate (%E) of the whey protein films. The 10% whey protein films had the highest WVP (28.73 g·mm/ kPa·day·m^2) and TS (1.85±0.11 Mpa). But, in this case, an increase of WVP was caused by the thickness of whey protein films. At the concentration of 8% whey protein, appropriate thickness was obtained. Whey protein films prepared at the pH 6.75 and 95°C showed lower WVP (28.38 g·mm/ kPa·day·m^2) and elongation rate (12.9%) and higher TS value (3.769±0.407 MPa) than at the pH 6.75 and 75°C. As the temperature increased, WVP of films decreased slightly and tensile strength increased slightly, while elongation rate decreased significantly. Higher WVP and TS were observed at pH 6.75 compared to pH 7-9. In contrast, significantly higher elongation was observed at pH 9 compared to pH 6.75-8. Among the plasticizer types used, the addition of sorbitol showed the highest TS value (6.244±0.297 MPa) at the concentration of 0.4 g sorbitol and elongation rate (49%) at the concentration of 0.6 g sorbitol.

Key words: whey protein, water vapor permeability, tensile strength, elongation rate

INTRODUCTION

It is estimated that approximately 14 million kg of sweet cheese were produced in Korea in 1996. The generation of whey from cheese production could be estimated about 180 millions tons of whey fluid in 1996. Some of whey is used for human food and animal feed applications. Manufacturing of edible films from whey protein products might represent an effective means of utilization of excess whey [1]. The formation of the heat-induced gel structure involves a complex series of chemical reactions involving dissociation, denaturation and exposure of hydrophobic amino acid residues. These reactions are influenced by experimental conditions such as protein concentration, pH, heating temperature and ionic strength [2]. These films gave the potential to control mass transfer and extended food shelf life [3]. Although many studies have been conducted on the thermal denaturation of this protein, complete comprehension of film property on the influence of pH, temperature, and plasticizers is insufficient. An objective of this study was the production of edible film as the effective means of utilization of excess whey. We have examined the effects of pH, temperature, and plasticizers on WVP, TS, and Elongation rate of the films.

MATERIALS AND METHODS

Film Materials

Whey protein concentrates(WPC) used to make films was supplied by Land O'Lakes, Inc.(Mineapolis, MN). Sorbitol, glycerol and polyethylene glycol were used as plasticizers. Lithium chloride and magnesium nitrate were used for adjustment of relative humidity.

Film Production

Whey protein concentrate (WPC) solutions (4-10%, W/V) were prepared and heated between 75 and 95°C for 10 min with stirring on a hot plate (PC-101, Corning incorporated, NY). Resulting solutions were slowly cooled in a cold storage room (4°C) and were vacuumed to remove dissolved air. The weights of glycerol, polyethylene glycol or sorbitol relative to the weight of WPC were then added as plasticizers. The solutions were spread evenly onto a 30×30 cm, rimmed, teflon plate resting on leveled glass surface. These plates were allowed to dry for approximately 18 hr at room temperature. Dried films were then peeled from the casting surface.

Thickness Measurement

Film thickness was measured to 1 μm (0.001 mm) level with micrometer (SM-1201, Teclock corporation, Japan).

Water Vapor Permeability (WVP)

Water vapor transmission rate (WVTR) was determined gravimetrically using a variation of the ASTM E96-90 Standard Method [4], known as the cup method.

Tensile Strength (TS) and Elongation Rate (%E)

TS and %E were evaluated with Instron (RTM-500.

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Orientec corporation, USA) according to the ASTM Standard Method E882-88 [5].

RESULTS AND DISCUSSION

Effects of WPC Concentration

In this study, we examined the effects of the whey protein concentration on physical properties of whey films (Table 1). A significant difference was observed in the WVP property of films formed from 6% to 10% WPC solutions heated at 76°C for 10 min. Below 6%, whey films were not formed, presumably due to lack of intermolecular interactions upon film dehydration. As the concentration of whey protein increased, the WVP and TS of whey protein films increased, and while the elongation had no variation. The 10% whey protein films had the highest WVP (28.73 g·mm/kPa·day·m^2) and TS (1.85±0.11 Mpa). But, in this case, an increase of WVP was caused by the thickness of whey protein films. Many edible films are hydrophilic in nature, resulting in the characteristic thickness effect for whey protein films. Because of the hydrophilic property of edible films, the film's WVP is very high. This high WVP property is a point of weakness. Ideal polymeric films exhibit no thickness effect on WVP. However, the hydrophilic films often exhibit positive slope relationships between thickness and water vapor permeability [6]. In a previous studies, several explanations have been provided for such thickness effects. It was reported that thickness effects occur from the film swelling as a result of attractive forces between films and water. Such film swelling should result in varying film structures [7]. Another researcher proposed that thickness effect results from the interactions of permeating water molecules with polar groups in the film structure [8]. Therefore, WVP values reported in this study applied only to the specific experimental conditions (88% relative humidity gradient and 25°C).

Effects of Heat Treatment

Heat treatment was necessary for the formation of whey protein based edible films. Without heat treatment, such films cracked into small pieces when dried, due to lack of intermolecular interations. Heating unfolds protein chains exposing sulfhydryl and hydrophobic groups. The existence of thiol groups is of importance for changes occurring in solution during heating, as it is involved in reactions with other proteins [9]. The effects of heat treatment and pH on the WVP, TS, and elongation rate of whey protein films were examined (Table 2 and Fig. 1). Whey protein films prepared at the pH 6.75 and 95°C showed lower WVP (28.38 g·mm/kPa·day·m^2) and elongation rate (12.9%) and higher TS value(3.769±0.407) than at the pH 6.75 and 75°C. As the temperature increased, WVP and elongation rate values decreased, while TS values increased. The decrease of WVP is expected to be caused by film structure changes. These conformational changes could be due to dimer formation between whey protein fractions or to aggregates formation [10]. At higher temperature, more tight structure resulted in lower WVP and higher TS of whey protein films.

Table 2. Effects of heat treatment and pH on water vapor permeability of whey protein films

pH	Heat temperature	Thickness[a] (mm)	Water vapor permeability[a] (g·mm/kPa·day·m^2)
pH 6.75	75°C	0.123	36.70
	80°C	0.118	35.62
	85°C	0.120	38.12
	90°C	0.110	30.24
	95°C	0.117	28.38
pH 7	75°C	0.121	36.88
	80°C	0.114	34.08
	85°C	0.118	34.27
	90°C	0.125	32.28
	95°C	0.119	31.55
pH 8	75°C	0.122	34.45
	80°C	0.113	32.98
	85°C	0.114	32.76
	90°C	0.124	31.55
	95°C	0.114	25.58
pH 9	75°C	0.114	31.06
	80°C	0.122	30.13
	85°C	0.120	28.52
	90°C	0.109	29.82
	95°C	0.113	25.76

[a]Thickness, WVP, TS, and Elongation rate data are mean values
[b]TS data are mean values±standard deviations

Effects of pH

When whey protein solutions were adjusted to various pH(4-12), we could observe that films were formed at pH 6.75 to pH 9. To examine the physical properties of the film, we performed WVP, TS, and elongation rate tests. As shown in Table 2 and Fig. 1, higher WVP and TS values were observed at pH 6.75. In contrast, the significantly higher elongation rate was observed at pH 9. And while, in the case of low pHs (4, 5, and 6), whey protein solutions were not formed to films because of precipitation of whey protein. A similiar observation, the lack of film formation at the isoelectric region of the protein, was reported for soy protein-lipid films formed on the surface of heated soy milk. This lack of film formation occurs from three dimensional changes of proteins resulting from the changes of intermolecular covalent disulfide, hydrophobic and hydrogen bonds [11]. Also, whey protein solutions of high pHs (10, 11, and 12)

Table 1. Effects of protein concentration in the film forming solution (heated at 7.5°C for 10 min) on water vapor permeability, tensile strength, and elongation rate

Protein conc.	Thickness[a] (mm)	WVP[a] (g·mm/kPa·day·m^2)	Tensile strength[a,b] at break (MPa)	Elongation rate[a] (%)
6% whey protein	0.095	16.25	1.39±0.13	36
8% whey protein	0.111	20.70	1.67±0.13	32
10% whey protein	0.146	28.73	1.85±0.11	32

[a]Thickness, WVP, TS, and Elongation rate data are mean values
[b]TS data are mean values±standard deviations

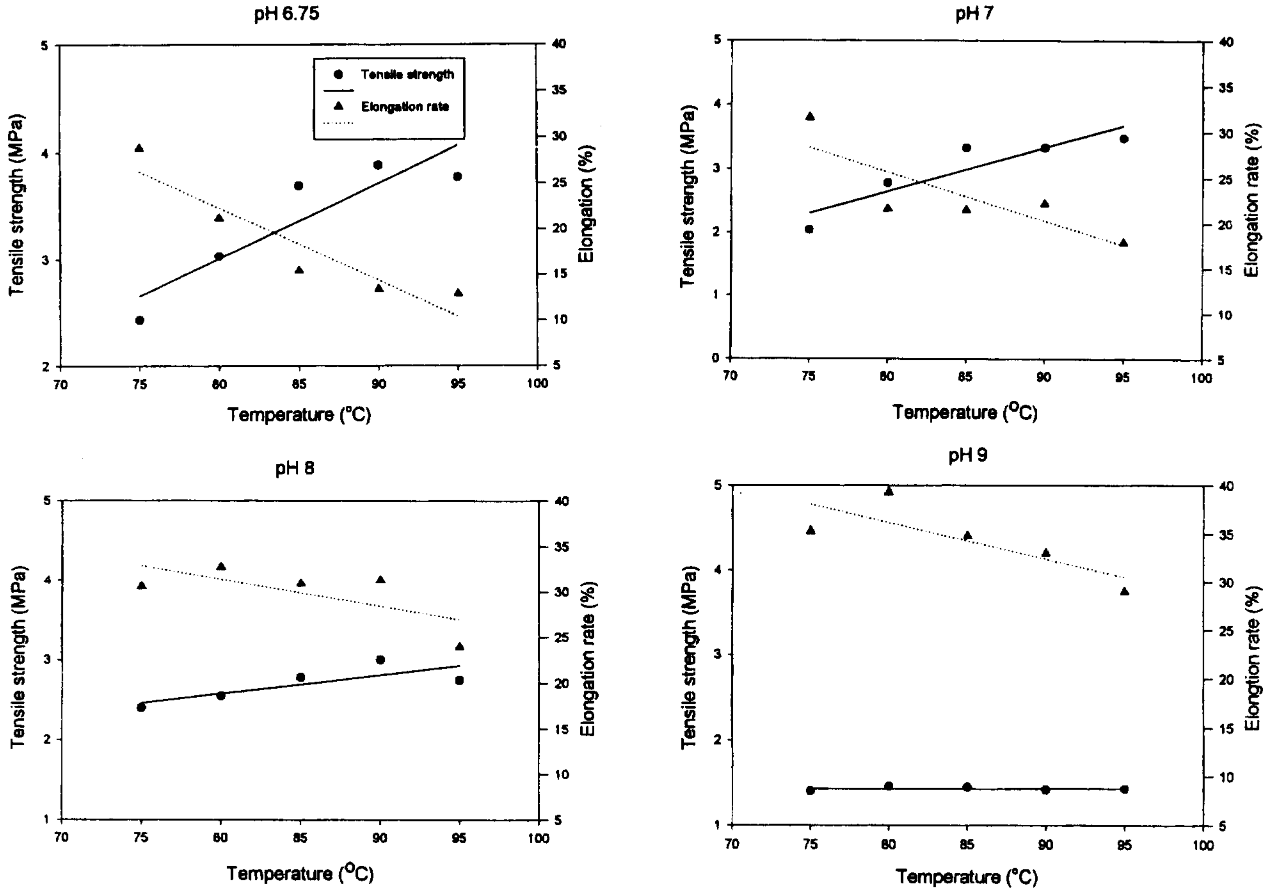

Fig. 1. Effects of heat treatment and pH on tensile strength and elongation rate of whey protein films.

had not been formed to films. Most likely, strong repulsive forces between highly negative charges of protein chains prevent protein molecules form associating. Therefore, we considered that the pH of the whey protein solution played a role as important factor in the physical properties of whey protein films.

Effects of Plasticizer Types and Concentrations

Plasticizers are frequently added to make flexible films. Use of plasticizer increases WVP because of the disruption of hydrogen bonds among the polymer chain [12]. To examine the effects of different types of plasticizers on the film physical properties, three types of plasticizers were used (Table 3, 4). Edible films plasticized by sorbitol exhibited significantly the highest TS value (6.244±0.297) at the concentration of 0.4 g sorbitol and elongation rate (49%) at the concentration of 0.6 g sorbitol among the plasticizers (Table 3). On the other hand, edible films plasticized by PEG300 ex-

Table 3. Effects of plasticizer types and concentrations on the tensile strength and elongation rate of whey protein films

Plasticizer types	WPC:Plasticizer	Thickness[a] (mm)	Tensile strength[a,b] at break (MPa)	Elongation rate[a] (%)
Sorbitol	1:0.2	c	c	c
	1:0.4	0.119	6.244±0.297	10.4
	1:0.6	0.110	2.165±0.065	49
	1:0.8	0.103	0.788±0.048	40
	1:1.0	0.117	0.320±0.044	41
Glycerol	1:0.2	c	c	c
	1:0.4	0.087	3.703±0.084	10
	1:0.6	0.082	0.956±0.034	24
	1:0.8	0.093	0.415±0.064	32
	1:1.0	p	p	p
Polyethylene glycol	1:0.2	c	c	c
	1:0.4	c	c	c
	1:0.6	c	c	c
	1:0.8	m	m	m
	1:1.0	m	m	m

[a]Thickness, TS, and Elongation rate are mean values, [b]TS data are mean values±standard deviations, [c]Cracked films, [p]No peeling, [m]Crackable structure.

Table 4. Effects of plasticizer types and concentrations on water vapor permeability of whey protein films

Plasticizer types	WPC: Plasticizer	Thickness[a] (mm)	Water vapor permeability[a] (g·mm/kPa·day·m^2)
Sorbitol	1:0.2	0.076	20.30
	1:0.4	0.103	27.19
	1:0.6	0.115	26.61
	1:0.8	0.101	31.89
	1:1.0	0.088	37.39
Glycerol	1:0.2	c	c
	1:0.4	0.089	21.49
	1:0.6	0.105	24.63
	1:0.8	0.100	32.13
	1:1.0	p	p
Poly-ethylene glycol	1:0.2	c	c
	1:0.4	c	c
	1:0.6	0.104	19.89
	1:0.8	0.107	21.70
	1:1.0	m	m

[a]Thickness and WVP data are mean values, [c]Cracked films, [p]No peeling, [m]Crackkable structure.

hibited lower WVP value (21.70 g·mm/kPa·day·m^2) than edible film plasticized by sorbitol (31.89 g·mm/kPa·day·m^2) or glycerol (32.13 g·mm/kPa·day·m^2) at the cocentration of 0.8 g plasticizer (Table 4). Also edible film plasticized by PEG300 formed a crakable structure. As the sorbitol concentration increase, TS significantly decreased, WVP values significantly increased. However, elongation rate had no variation above the 0.6 g sorbitol.

This could be explained by possible reduction of hydrogen bonds between macromolecules in amorphous region of proteins. It was reported that the small molecular weight plasticizers were more effective than the large molecular weight plasticizers because these plasticizers easily incorporate into protein chains and result in formation of hydrogen bonds between these hydroxyl group of plasticizer and amide groups of protein [7]. Glycerol has smaller molecular weight than sorbitol. However, the tensile strength and elongation rate of the whey protein film plasticized by glycerol were lower than that plasticized by sorbitol. It was considered that the glycerol resulted in the excessive disruption of hydrogen bonds and hydrophobic interactions between whey protein molecules.

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