Mechanical Properties and Water Vapor Permeability of Edible Films from Whey Protein Isolate and Sodium Dodecyl Sulfate

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The ability of sodium dodecyl sulfate (SDS) to plasticize edible films from whey protein isolate (WPI) was assessed. SDS was not able to plasticize WPI films on its own, but it was an effective coplasticizer in films containing either sorbitol or glycerol as the main plasticizer. In films that contained sorbitol, a mass ratio of SDS to WPI ($R_{S:W}$) of 0.2 resulted in films that were more extensible and more soluble but with almost unchanged water vapor permeability (WVP). In films that contained glycerol, the same $R_{S:W}$ resulted in less extensible and soluble films with slightly higher WVP values. Values of $R_{S:W} > 0.3$ resulted in antiplasticization, although there was a reduction in WVP. At $R_{S:W} > 1$ films were so brittle that they could not be handled without breaking. The mechanical properties of WPI films that contained SDS were comparable to published values for other proteinaceous, edible films.

Keywords: *Plasticizer; Young's modulus; tensile strength; protein/surfactant interactions*

INTRODUCTION

Proteinaceous, edible films are excellent barriers to the transport of gas and moderate barriers to the transport of moisture (Krochta, 1992). Most proteins form films that are brittle, so a plasticizer is essential (Guilbert, 1986). Compounds such as glycerol, sorbitol, and poly(ethylene glycol) are widely used (Guilbert, 1986). Plasticizers are thought to disrupt hydrogen bonding between neighboring protein strands, so that interchain attractive forces are reduced and chain mobility is increased (Guilbert, 1986; Kester and Fennema, 1986). As chain mobility increases, diffusion coefficients also increase, resulting in higher gas and water vapor permeabilities. However, the mechanisms of action of these plasticizers are poorly understood, and no basic studies have been reported. It is often necessary to add a large amount of plasticizer to obtain a film that can be handled easily. Films based on whey protein isolate, for example, must comprise 25−50% plasticizer on a dry weight basis (McHugh et al., 1994; McHugh and Krochta, 1994). An alternative plasticizer is strongly needed that can be added at low levels and that will improve flexibility without unduly compromising barrier properties.

Surfactants have received little attention as potential plasticizers. Most surfactants that have been tested have been reported to be ineffective (Gontard et al., 1994). Nevertheless, ionic surfactants have the potential to act as plasticizers by disrupting hydrogen bonding and by increasing the charge repulsion between neighboring protein molecules.

The anionic surfactant sodium dodecyl sulfate (SDS) has been widely studied because of its ability to denature, and associate with, a wide variety of proteins. Proteins have strong specific and nonspecific interactions with SDS, which can yield information about the conformation and function of the protein molecule and its various domains. Of the whey proteins, bovine serum albumin (BSA) has been studied the most (Moriyama et al., 1993). The interaction between SDS and BSA can be divided into two regions (stoichiometric and co-operative) which are defined by the number of SDS molecules, n, bound per BSA molecule (Yamasaki et al., 1992).

In the stoichiometric binding region [$1 < n < 10-12$ (Enescu et al., 1993; Yamasaki et al., 1992)] the BSA molecule becomes more compact and stiff (Enescu et al., 1993) and more resistant to denaturation by heat (Yamasaki et al., 1992) and by urea (Moriyama et al., 1993).

Co-operative binding is weaker than stoichiometric, and it has two subregions. At $10-12 < n < 80$, SDS forms micelle-like complexes with the protein (Enescu et al., 1993; Yamasaki et al., 1992) that can solubilize hydrophobic molecules such as Nile Red dye (Daban et al., 1991). There are pronounced changes in secondary and tertiary structure (Takeda and Moriyama, 1990; Takeda et al., 1992), and the hydrodynamic radius increases from 3.1 to 6.0 nm as n goes from 0 to 50 (Takeda et al., 1992). It does not increase further as n increases to 100.

In the second co-operative binding subregion ($80 < n < 180$) SDS molecules enter sites that have been exposed as the surfactant denatures the protein (Enescu et al., 1993). The limit of n is 180−200, when the protein is saturated with SDS and micelles begin to form in the bulk solution (Enescu et al., 1993; Moriyama et al., 1993). This implies that BSA can bind up to 0.9 g of SDS/g of protein, which is rather lower than the widely quoted 1.4 g bound reported by Reynolds and Tanford (1970).

The binding regimes of the other major whey proteins (β-lactoglobulin, α-lactalbumin, and immunoglobulin G) have not been determined in such detail, but it seems reasonable to assume that they follow a similar pattern of stoichiometric and co-operative binding, but with different values for n. SDS forms micelle-like complexes with β-lactoglobulin (Imamura and Konishi, 1992), which results in an increase in α-helix and a decrease

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in β-sheet and random coil (Takeda and Moriyama, 1989). Addition of SDS to α-lactalbumin causes an increase in α-helix, near elimination of β-sheet, and a small decrease in random coil (Takeda and Moriyama, 1990). Such changes in secondary structure would also be expected to affect tertiary structure.

In addition to affecting protein structure, SDS also affects the interactions between neighboring protein molecules, through charge repulsion and altered hydrophobic interactions. SDS thus has profound effects on the properties of whey protein solutions and gels (McClements et al., 1993). Therefore, it is reasonable to expect that there will be some effect on the properties of protein films with added SDS. The objective of this paper was to investigate the potential of SDS to plasticize films based on whey protein isolate, through protein−surfactant interactions.

MATERIALS AND METHODS

Materials. Whey protein isolate (WPI; >95% protein on a dry weight basis) was obtained from Le Sueur Isolates, Le Sueur, MN. Sodium azide (>99%) was obtained from Sigma Chemical Co., St. Louis, MO. Sodium dodecyl sulfate, magnesium nitrate, sorbitol, and glycerol (all >99%) were obtained from Fisher Scientific, Fair Lawn, NJ.

Film Forming Solution. Preliminary experiments showed that SDS alone could not plasticize WPI films effectively. Therefore, solutions were prepared that contained WPI, SDS, and either sorbitol or glycerol as coplasticizer. The mass ratio of coplasticizer to protein was kept constant at 1/3. The mass ratio of SDS to protein, $R_{S:W}$, was varied over the range 0−0.2 in films that contained sorbitol. This range was designed to examine the effect of additions of small amounts of SDS, analogous to the amounts typically added in experiments with solutions and gels. The mass ratio of SDS to protein was varied over the range 0−1.0 in films that contained glycerol. This range was designed to determine the maximum amount of SDS that could be added to the system without weakening the films too much. Solutions of WPI (10.00 wt %), sodium azide (0.02 wt %), and SDS were degassed and heated, with stirring, to 90 °C. After 30 min, they were cooled to room temperature and either sorbitol or glycerol was added.

Film Formation. Aliquots of film forming solution (∼20 g) were weighed onto smooth, circular, rimmed plates (14.7 cm i.d.; ultrahigh molecular weight, high-density polyethylene) to obtain 3.0 g of solids per plate. The solutions were spread out to cover each plate, using a bent glass rod. The solutions were left to dry into films overnight on level aluminum slabs, at room temperature (about 20 °C).

Mechanical Properties (Tensile Tests). Films plasticized with glycerol were tested using a different Instron facility from that used for the films plasticized with sorbitol, because access to a superior testing facility became available during the course of the study. This facility had better climate control and better capabilities for sample preparation and handling than the facility used to test the films plasticized with sorbitol. The procedures for sample preparation and testing therefore varied slightly between the two facilities.

Films Plasticized with Sorbitol. Test pieces were cut by hand from films plasticized with sorbitol. The films had to be softened prior to sample preparation to prepare test pieces with the smooth, straight edges that are necessary for tensile testing. Films were softened by conditioning at ∼90% relative humidity (RH) in a chamber that contained distilled water and a small fan to circulate air. Test pieces of film, each 15−16 mm wide and 100−125 mm long, were cut using a razor blade and steel-edged ruler. Both ends of each piece were carefully attached to separate poly(methyl methacrylate) strips using double-stick tape. The plastic strips allowed the test pieces to be aligned accurately in the jaws of the Instron grips, which were custom-made in the workshop at the Department of Food Science at the University of California, Davis. The strips also helped to prevent the test pieces from failing prematurely in the jaws of the grips. The assembled test pieces were then prepared for testing by conditioning to 50% RH in a chamber that contained saturated magnesium nitrate solution, for at least 24 h. The thickness of each sample was taken as the average of five measurements made at random points on the equilibrated sample. Measurements were made to the nearest 0.0001 in. using a micrometer (Model 7326, Mitutoyo Corp., Japan). Samples were tested on an Instron Universal Testing machine (Model 1122, Instron Corp., Canton, MA), in a room at 23 ± 2 °C and 50 ± 5% RH. A 1962 N (200 kg) load cell was used. The gauge length was 90 mm and the rate of grip separation was 50 mm min^{-1}. Tensile properties were calculated from the curve of stress (tensile force/initial cross-sectional area) versus strain (extension as a fraction of the original length), using Series IX Automated Materials Testing System software (Instron). The following parameters were calculated: Young's modulus (i.e. the elastic modulus), stress and strain at yield (the point where the slope of the force/extension curve is zero), and stress and strain at break (the point where the sample breaks and the force drops to zero). At least 14 replicates were tested for each film formulation.

Films Plasticized with Glycerol. Test pieces were punched out of films that contained glycerol using a 25.4 mm × 152.4 mm (1 in. × 6 in.) die in a hand-operated press. The use of a die and press made it unnecessary to soften the films prior to sample cutting. Optimum samples were obtained by conditioning the films in a controlled environment room at 23 ± 2 °C and 65 ± 2% RH for 24 h prior to sample preparation. Test pieces were conditioned in the same room for at least 1 week before testing. The thickness of each piece was taken as the average of six measurements at random points on the equilibrated sample using the micrometer described above. Samples were tested on an Instron Universal Testing machine (Model 1122) in a controlled environment room at 23 ± 2 °C and 65 ± 2% RH. It was not possible to adjust the RH to match that used in the tests on films containing sorbitol. An 890 N (200 lb) load cell was used with self-aligning grips and 25.4 mm × 50.8 mm (1 in. × 2 in.) stainless steel faces (Instron). The use of self-aligning grips obviated the need for poly(methyl methacrylate) strips and double-stick tape. The gauge length was 101.6 mm (4 in.), and the rate of grip separation was 50 mm min^{-1}. Tensile properties were calculated using Series IX Automated Materials Testing System software (Instron). Between 15 and 27 replicates were tested for each film formulation.

Water Vapor Permeability (WVP). The WVP of each film was determined according to the WVP correction method of McHugh et al. (1993) using distilled water. Six replicates were examined for each film formulation. The thickness of each replicate was taken as the average of five measurements at random points on the film, gathered immediately after WVP determination, using the micrometer described above.

Solubility. The percentage of dry matter in the films that could be extracted into water over a 24 h period was determined according to the method of Gontard et al. (1994). Three replicates were measured for each film.

RESULTS AND DISCUSSION

Calculation of Number of SDS Molecules Bound per Molecule of WPI. In the systems studied here, n can be calculated by multiplying $R_{S:W}$ by MW_{WPI}/MW_{SDS}, where MW is molecular weight and the subscripts WPI and SDS have their usual meaning. The molecular weight of SDS is 288.38, and the molecular weight of WPI was calculated as a weighted average of 24 000, using the molecular weight and relative content of the component proteins. Using these values of molecular weight, values of n ranged from 0 to 16 for the films that contained sorbitol and from 0 to 83 for the films that contained glycerol. Thus, films that contained sorbitol spanned the stoichiometric binding regime (assuming that the other components of WPI behaved

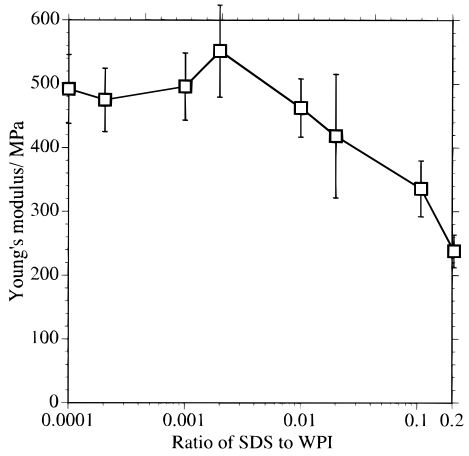

Figure 1. Young's modulus *vs* mass ratio of SDS to WPI in edible films containing sorbitol. Bars represent standard deviation.

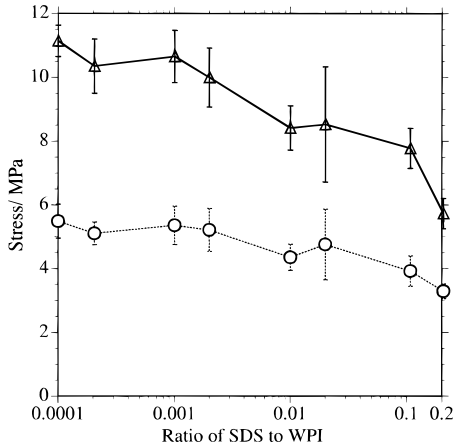

Figure 2. Yield stress (△) and breaking stress (○) as a function of the mass ratio of SDS to WPI in edible films containing sorbitol. Bars represent standard deviation.

similarly to BSA); films that contained glycerol spanned the stoichiometric binding region and the micelle complex part of the co-operative region.

Films Plasticized with Sorbitol. Up to $R_{S:W} \sim 0.02$ ($n \sim 1.7$), addition of SDS to films plasticized with sorbitol had no effect on Young's modulus (Figure 1), yield stress, or breaking stress (Figure 2). Above this ratio there was a moderate plasticizing effect, which was most evident in the drop in Young's modulus and yield stress (Figures 1 and 2). The breaking stress also fell as $R_{S:W}$ rose, but not as markedly (Figure 2). The breaking strain appeared to drop and then increased as $R_{S:W}$ was increased (Figure 3). However, there was a high degree of variability in the data due to premature failure in several samples. The yield strain was largely insensitive to the amount of SDS in the film. It increased slightly as $R_{S:W}$ rose above 0.1 ($n \sim 8.3$; Figure 3).

Thus, it was only necessary to bind two or three SDS molecules per molecule of WPI to have a small effect on mechanical properties. Binding of 8−16 SDS molecules per molecule of WPI was necessary to observe the significant decreases in Young's modulus and breaking stress (and increase in elongation at break) that are indicative of plasticization. The water vapor permeability of the film was almost independent of $R_{S:W}$ (Figure 4), so plasticization was achieved without compromising barrier properties. SDS was an effective coplasticizer when used in conjunction with sorbitol.

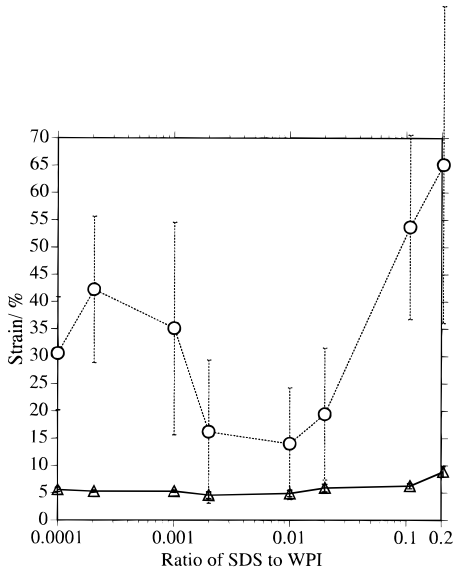

Figure 3. Yield strain (△) and breaking strain (○) as a function of the mass ratio of SDS to WPI in edible films containing sorbitol. Bars represent standard deviation.

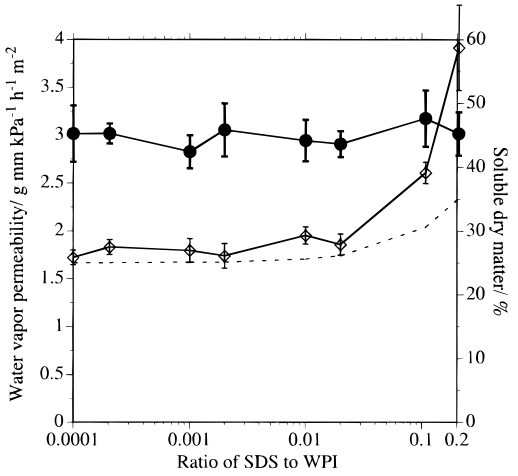

Figure 4. Water vapor permeability (●) and solubility (◇, expressed as percentage of the dry matter that could be extracted into water) *vs* mass ratio of SDS to WPI in edible films containing sorbitol. The dotted line indicates the percentage of the dry matter made up of sorbitol and SDS. Bars represent standard deviation.

The solubility of the film was unchanged up to $R_{S:W} = 0.02$ ($n \sim 1.7$; Figure 4). The constant value of ~25% suggested that the sorbitol and SDS (which comprised ~25% of the film) could be extracted into water. The solubility increased sharply at $R_{S:W} > 0.02$ ($n > 1.7$), which suggested that the normally insoluble protein matrix was partially solubilized. WPI films are insoluble because of extensive intermolecular disulfide bonding (McHugh and Krochta, 1994). The presence of SDS appeared to affect the extent of disulfide bonding sufficiently to increase solubility. SDS may have been bound to amino acid residues close to sulfur-containing amino acids and thus sterically inhibited the formation of intramolecular disulfide bonds.

Films Plasticized with Glycerol. Films prepared with glycerol could tolerate very high amounts of SDS without losing structural integrity. Although films could be formed with $R_{S:W} \leq 1.5$ ($n \leq 125$), only films with $R_{S:W} \leq 1$ ($n \leq 83$) were strong enough to be handled. This value of n corresponds roughly with the upper limit of the first co-operative binding subregion. The addition of SDS affected films that contained

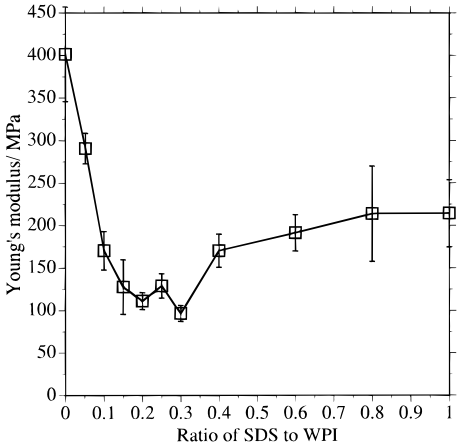

Figure 5. Young's modulus *vs* mass ratio of SDS to WPI in edible films containing glycerol. Bars represent standard deviation.

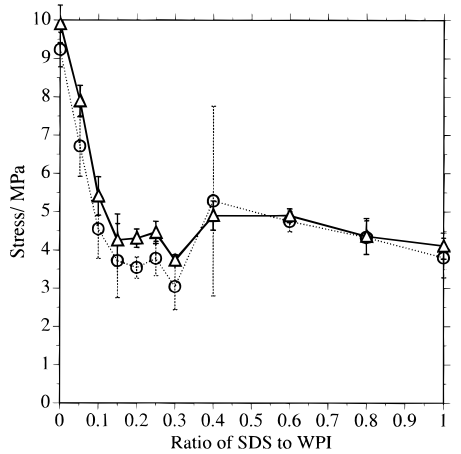

Figure 6. Yield stress (△) and breaking stress (○) as a function of the mass ratio of SDS to WPI in edible films containing glycerol. Bars represent standard deviation.

glycerol more than it did films that contained sorbitol. Some differences were expected because the films plasticized with glycerol were tested at a slightly higher relative humidity than those plasticized with sorbitol. Films were prepared using equal mass ratios of sorbitol or glycerol to whey protein isolate. Thus, films plasticized with glycerol contained more plasticizer on a mole for mole basis than did films plasticized with sorbitol, because the molecular weight of sorbitol (182.17) is almost exactly twice that of glycerol (92.09). This may also account for the heightened effect of SDS on the mechanical properties of films prepared with glycerol.

Young's modulus was reduced twice as much at $R_{S:W} = 0.2$ ($n = 17$; Figure 5). Young's modulus had a minimum at $R_{S:W} = 0.3$ ($n = 25$) and tended toward a value of ~200 MPa as $R_{S:W}$ tended toward 1 ($n = 83$). Films that contained glycerol had a much smaller difference between values of yield stress and breaking stress than did films that contained sorbitol (Figure 6). The variation in both quantities with $R_{S:W}$ followed a pattern very similar to that seen in Young's modulus. Young's modulus, yield stress, and breaking stress all changed most dramatically over the stoichiometric regime ($0 < R_{S:W} < 0.2-0.3$). Changes over the cooperative binding regime ($R_{S:W} > 0.2-0.3$) were less dramatic and reflected the mechanical properties of the SDS itself, besides the modification of the properties of the WPI. Films that contained glycerol were less

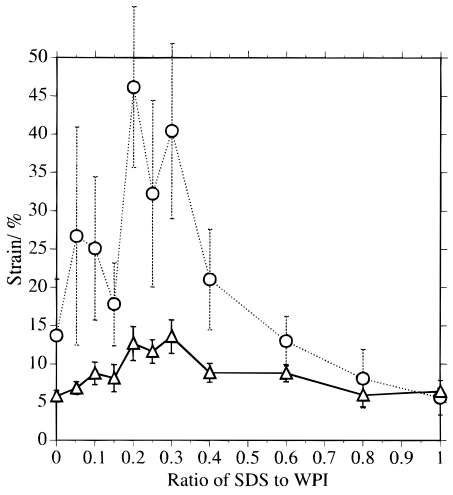

Figure 7. Yield strain (△) and breaking strain (○) as a function of the mass ratio of SDS to WPI in edible films containing glycerol. Bars represent standard deviation.

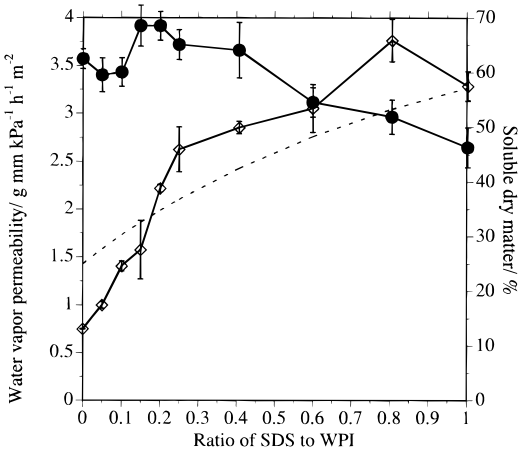

Figure 8. Water vapor permeability (●) and solubility (◇, expressed as percentage of the dry matter that could be extracted into water) *vs* mass ratio of SDS to WPI in edible films containing glycerol. The dotted line indicates the percentage of the dry matter made up of glycerol and SDS. Bars represent standard deviation.

extensible than films that contained sorbitol (Figure 7). Both breaking strain and yield strain peaked at $R_{S:W} \sim 0.25-0.30$ ($n \sim 20-25$; Figure 7). Breaking strain dropped sharply as $R_{S:W}$ rose above 0.4 ($n = 33$), which indicated antiplasticization.

The WVP was slightly depressed at $R_{S:W} < 0.15$ ($n < 12$) and elevated at $0.15 \leq R_{S:W} \leq 0.3$ ($12 \leq n \leq 25$; Figure 8). At $R_{S:W} > 0.3$ ($n > 25$) the WVP dropped, which was probably due to a contribution from the large hydrophobic moieties of the SDS molecules. SDS was an effective coplasticizer when used with glycerol, provided that $R_{S:W}$ was below 0.3, so that binding fell within the stoichiometric regime.

The solubility of films that contained glycerol was less than half that of films that contained sorbitol at $R_{S:W} \leq 0.2$ ($n \leq 17$; Figure 8), which was puzzling, given the high solubility of SDS and the excellent miscibility of glycerol and water. Solubility increased markedly as $R_{S:W}$ increased from 0 to 0.3 ($n = 25$) and then increased more slowly as $R_{S:W}$ increased from 0.3 to 1 ($n = 25-83$). The values of solubility at $R_{S:W} > 0.2$ were consistent with extraction of the SDS and glycerol, and some of the protein as well. It appeared that disulfide bonding was inhibited in the films containing glycerol as well as in the films containing sorbitol.

Table 1. Comparison of Some Mechanical Properties from the Present Study with Reported Values for Edible Films Based on Milk Proteins[a]

study	composition	puncture stress, MPa	tensile stress, MPa	elongation, %	yield stress, MPa	Young's modulus, MPa
Banerjee and Chen (1995)	sodium caseinate:gly 2:1	1.92	2.98[p]	29.89		
	calcium caseinate:gly 2:1	5.44	4.25[p]	1.45		
	potassium caseinate:gly 2:1	2.03	2.97[p]	42.8		
	WPC:gly 2:1	1.69	3.36[p]	20.84		
	WPI:gly 2:1	2.80	5.94[p]	22.74		
Chen et al. (1993)	WPI:gly 2:1	3.05 ± 0.56	5.94 ± 0.32[p]			
Habig-McHugh and Krochta (1994)	WPI:gly 2.3:1		13.9[b]	30.8[b]		
	WPI:sorb 2.3:1		14.0[b]	1.6[b]		
	WPI:sorb 1:1		14.7[b]	8.7[b]		
	WPI:gly 5.7:1		29.1[b]	4.1[b]		
this work	WPI:sorb 3:1		4.5 ± 0.7[b]	21.2 ± 12.6[b]	8.6 ± 1.4	442 ± 60
	WPI:gly 3:1		9.2 ± 0.5[b]	13.7 ± 7.4[b]	9.9 ± 0.5	401 ± 56
Maynes and Krochta (1994)	TMP-LUF:gly 3:1		10.0[b]	5.2[b]		70.7
	TMP 1100:gly 3:1		8.6[b]	22.1[b]	9.5	59.3
	TMP 1230:gly 3:1		9.1[b]	33.3[b]	13.3	67.9
	TMP 1350:gly 3:1		6.3[b]	38.5[b]	5.9	41.6

[a] All films were prepared by casting. The superscripts p and b refer to stresses and elongations and peak and at break, respectively. gly, glycerol; sorb, sorbitol; WPC, whey protein concentrate; WPI, whey protein isolate; TMP-LUF, total milk protein, prepared in laboratory by ultrafiltration; TMP 1100, TMP 1230, TMP 1350, commercial total milk protein.

Films that contained glycerol were less extensible and more permeable than films that contained sorbitol over the range $0 < R_{S:W} \leq 0.2$. This is consistent with previous observations that, weight for weight, sorbitol is a more effective plasticizer than glycerol (McHugh and Krochta, 1994). Taking into account the greater molecular weight of the sorbitol, it is an even more effective plasticizer on a mole for mole basis. The effects of SDS on mechanical properties, although significant, are not sufficiently strong to outweigh the underlying differences between the two major plasticizers.

Effectiveness of SDS as a Plasticizer. SDS has a pronounced effect on the conformation of WPI in solution, and it reduces gel strength substantially (McClements et al., 1993). Gel formation is completely suppressed at $R_{S:W} > 0.05$ ($n > 4$) (McClements et al., 1993). However, SDS was not effective as a plasticizer when used on its own in WPI films. Gontard et al. (1994) also reported that glycerol monostearate, acetic ester of monoglyceride, sucrose ester of stearic acid, and diacetyl tartaric ester of monoglyceride had no substantial plasticizing effect on gluten films. It is not clear why SDS and other surfactants cannot plasticize films effectively on their own. There are at least two possible reasons for the poor plasticizing ability of SDS compared to polyols such as sorbitol and glycerol.

One possibility is that SDS requires the film to contain a certain minimum amount of water to be fully effective. Many of the effects of SDS in systems that contain water derive from altered hydrophobic interactions between the protein and the solvent. Edible films generally contain very low levels of moisture. Glycerol and sorbitol are humectants, and part of their plasticizing action derives from their ability to hold water (which itself is a very effective plasticizer) in the film.

Alternatively, it may be that surfactants, including SDS, simply do not disturb the attractive interchain forces in the film sufficiently to act as independent plasticizers. This would imply that they do not interfere very much with hydrogen bonding between neighboring protein chains.

Plasticization of Edible Films. It is useful to compare the mechanical properties of the films examined here with values reported in the literature. Mechanical properties of edible films are difficult to determine experimentally, because of difficulties in sample preparation and sensitivity to fluctuations in environmental factors such as relative humidity. Measurements on several different systems based on milk proteins are collated in Table 1. Comparison of measurements must be approached with caution because the sample dimensions, number of replicates, and test conditions varied from study to study. Nevertheless, it is clear that all of the systems based on milk protein yield films with comparable values of puncture stress, tensile stress, and elongation.

In fact, milk proteins, cereal proteins, soy protein, and collagen all yield films that have broadly similar mechanical properties (Krochta and de Mulder, 1995). Films from polysaccharides are rather stronger and more extensible than proteinaceous films (Krochta and de Mulder, 1995). Glycerol is the most widely used plasticizer in edible films. In all types of edible film, a small increase in glycerol level results in a large drop in tensile strength and an increase in elongation. In films from whey protein isolate, the relative effectiveness of plasticizers (as judged by their ability to increase extensibility) is given by sorbitol > glycerol ≫ SDS. Although SDS is less effective at modulating mechanical properties, it does have the advantage that it has less effect on WVP. Thus, SDS has potential for use as an adjunct to polyols for the plasticization of edible films from whey protein isolate.

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