

Mechanical and thermal properties of extruded soy protein sheets[☆]

J. Zhang, P. Mungara, J. Jane*

Department of Food Science and Human Nutrition & Center for Crops Utilization Research, Iowa State University, Ames, IA 50011, USA

Received 17 March 2000; received in revised form 11 August 2000; accepted 15 August 2000

Abstract

Soy protein plastic sheets were made by extrusion. The effects of water, glycerol, methyl glucoside, ZnSO₄, epichlorohydrin, and glutaric dialdehyde on the mechanical properties of soy protein plastic sheets were studied. The thermal transition temperatures and dynamic mechanical properties of soy protein plastics were also investigated. Depending on the moisture and glycerol contents, soy protein plastic sheets displayed properties from rigid to soft. The glass transition temperatures of the sheets varied from ca. -7 to 50°C with moisture contents ranging from 26 to 2.8% and 30 parts of glycerol. The soy protein plastic sheets were usually in their glassy states at room temperature unless they contained high moisture. The β-transitions of soy protein plastic sheets ranged from -33 to -72°C depending on the moisture. After being submerged in water for 20 h, the soy protein sheets absorbed up to 180% water. With the presence of two parts of ZnSO₄, water absorption of the soy protein sheets decreased by 30%. Soy protein sheets absorbed or lost moisture depending on the relative humidity of the environment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Soy protein plastics; Extrusion; Mechanical properties

1. Introduction

Petroleum-based plastics dominate today's plastics market because of their high strength, lightweight, low cost, easy processibility, and good water barrier properties. However, most of the synthetic polymers are not biodegradable. Synthetic biodegradable polymers, such as poly(lactic acid), polycaprolactone, and poly(hydroxy butyrate) have high production costs. With the increasing concerns of environmental pollution caused by non-biodegradable petroleum-based plastics, increasing efforts have been made to utilize the polymeric materials derived from agricultural products.

The United States is one of the major producers of soybeans in the world. Soybeans, a \$17.5 billion market in the United States, are mainly used for animal feeds. Soybeans contain approximately 42% protein, 20% oil, 33% carbohydrates, and 5% ash on a dry basis [1]. In addition to its use as a food ingredient, non-food applications of soy protein as polymeric materials have attracted increasing attention in recent years. The main attractive features of soy

protein-based plastics are that they are biodegradable, environmentally friendly, and from an abundant renewable resource. Use of soy protein as a plastic material can be traced back to the 1930s. Brother and Mckinney studied the formaldehyde-hardened soy plastics and their compounding with the phenolic resin [2,3]. The formaldehyde-treated soy plastics compounded with phenolic resin were reported to display very low water absorption.

In our laboratory, we studied the effects of pH [4], moisture content [4], processing conditions [4], cross-linking agents [5], and cellulose [5] (as a filler) on mechanical and physical properties of compression-molded soy plastics, and the morphology and biodegradation of soy protein-based plastics [6,7]. Effects of polyhydric alcohols as plasticizers on mechanical properties of soy protein-based plastics have also been studied and reported [8]. Otaigbe and Adams studied the composite of soy protein with polyphosphate, and their results showed enhanced strength, stiffness and improved water resistance [9].

It is well known that water plasticizes proteins and is critical for processing. Morales and Kokini studied the glass transition (T_g) of soy protein as a function of moisture content [10]. They reported that the T_g of conglycinin (7S) fraction ranged from 114 to -67°C with moisture content between 0 and 35%, whereas that of the glycinin (11S) fraction ranged from 160 to -17°C with moisture content between 0 and 40%. Kalichevsky et al. studied the glass

[☆] Journal Paper No. J-18788 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, Project No. 3258, and supported by Hatch Act and State of Iowa Funds.

* Corresponding author. Tel.: +1-515-294-9892; fax: +1-515-294-8181.
E-mail address: jjane@iastate.edu (J. Jane).

Table 1

Effect of glycerol concentration on mechanical properties of soy protein sheets (Formulation: SPI 610 (100 parts), H₂O (80 parts). Samples were equilibrated for 48 h prior to test)

Glycerol (parts)	σ_y^a (MPa)	σ_b^b (MPa)	P.E.Y. ^c (%)	P.E.B. ^d (%)	Strength (MPa)	E^e (MPa)	Toughness (MPa)
10	40.6 ± 2.5	40.6 ± 2.5	2.4 ± 0.5	3 ± 1	40.6 ± 1.0	1226 ± 85	0.4 ± 0.0
20	33.9 ± 0.8	29.6 ± 1.7	7.9 ± 0.4	74 ± 8	34.0 ± 0.8	1119 ± 70	21.2 ± 2.4
30	15.0 ± 0.9	14.0 ± 0.9	8.8 ± 0.2	133 ± 10	15.6 ± 0.4	374 ± 70	18.8 ± 1.6
40	1.6 ± 0.1	9.1 ± 0.2	2.5 ± 0.3	159 ± 12	9.1 ± 0.2	176 ± 12	13.0 ± 1.1
50	1.5 ± 0.1	7.1 ± 0.4	4.3 ± 0.5	185 ± 15	7.1 ± 0.4	144 ± 16	11.1 ± 1.3

^a σ_y is the stress at yield point.

^b σ_b is the stress at break point.

^c P.E.Y. is the percentage elongation at yield point.

^d P.E.B. is the percentage elongation at break point.

^e E is Young's modulus.

transition temperature of gluten and found that it was little affected by triolen, corn oil, and glycerol monostearate [11]. In this study, we investigated extrusion of soy plastic sheets and the plasticizing effects of water, glycerol, and methyl glucoside on mechanical and dynamic mechanical properties of soy protein plastics. We also investigated the cross-linking effects of soy protein by Zn⁺², a transition metal ion, and other cross-linking reagents.

2. Experimental

2.1. Materials

Soy protein isolate (SPI, Supro 760 and 610) was purchased from Protein Technologies International, St. Louis, MO, and used as received. It contained approximately 92% protein (dry basis), less than 1% carbohydrate, 4.7% moisture, and 4.0% ash. Glycerol and salts were reagent grade quality and were obtained from Fisher (Fisher Scientific, Pittsburgh, PA). Epichlorohydrin and glutaric dialdehyde were purchased from Aldrich (Aldrich Chemical Company, Milwaukee, WI). Methyl glucoside was a gift from Grain Processing Corporation (Muscatine, IA).

2.2. Compounding

SPI, water, glycerol, and other additives were thoroughly mixed in a high-speed mixer (Henschel Mixers American, Inc., Houston, TX). The general formulation of the soy protein sheets was SPI (100 parts), H₂O (60–90 parts), glycerol (20–50 parts), and other additives. The mixture was equilibrated overnight in a sealed plastic bag before compounding. The compounding extrusion was performed with a twin-screw co-rotating extruder (Leistritz Micro 18, American Leistritz Corp., Sommerville, NJ) equipped with an auto feeder. The diameter of the screw was 18 mm, and the length to diameter ratio (L/D) was 30. The screw speed was 150 rpm. The barrel of the extruder had five heating zones. The processing temperatures varied from 60 to 115°C depending on the formulation. The extrudate was pelletized, and the moisture content was determined.

2.3. Sheet extrusion

Soy protein sheets were extruded from above pellets using a single-screw extruder (C.W. Brabender Instruments, Inc., Hackensack, NJ) equipped with a 6-inch flat-sheet die. The barrel temperature varied from 120 to 160°C, and the die temperature was 100 to 120°C, depending on the formulation. The screw speed was 20–25 rpm. The sheet was drawn with a Brabender take-off unit. The thickness of the sheets ranged from 0.35 to 1.5 mm.

2.4. Mechanical properties

The sheets were cut into strips of 19 mm × 100 mm and dried at 50°C for 24 h. They were equilibrated at 50% relative humidity (RH) for 48 h right before testing and kept in sealed plastic bags till tests. Mechanical properties were measured using an Instron Universal Test Machine (Model 4502, Canton, MA) following the ASTM D882-91 method. The crosshead speed was 100 mm/min, and five replicates were tested for each sample.

2.5. Thermal analysis

Specimens with different moisture contents were prepared from the same batch of sheet samples by equilibrating them in separate chambers of different RH for 1 week. Saturated salt solutions of LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃, giving RH of 11, 32, 50, 75 and 93%, respectively, were used for this study. RH of 0% was achieved by placing P₂O₅ in a desiccator. Moisture contents of the equilibrated sheet samples were analyzed using a Perkin–Elmer thermogravimetric analyzer TGA-7 (Norwalk, CT). A sample (ca 10 mg) was scanned from 30°C at 20°C/min, and weight loss below 150°C was taken as the moisture content. Dynamic mechanical properties were measured on a Perkin–Elmer DMA-7 using a parallel plate measuring system. The sheet samples were shaped into a disk of about 7 mm in diameter and 1.3 mm in thickness. The temperature scan was from –100 to 130°C at 2°C/min, and the frequency of the dynamic force was 1 Hz. The static and dynamic forces were set at 300 and 330 dyn,

Table 2
Effect of methyl glucoside on mechanical properties of soy protein sheets (formulation: SPI 760 (100 parts), H₂O (80 parts))

Methyl glucoside (parts)	Glycerol (parts)	ZnSO ₄ (parts)	σ_y^a (MPa)	σ_b^b (MPa)	P.E.Y. ^c (%)	P.E.B. ^d (%)	Strength (MPa)	E^e (MPa)	Toughness (MPa)
0	30	1.0	12.0 ± 0.4	11.7 ± 1.8	9.9 ± 0.5	110 ± 5	12.8 ± 0.7	305 ± 23	13.2 ± 3.5
10	20	1.0	15.1 ± 0.1	14.3 ± 0.3	9.7 ± 0.8	125 ± 13	15.3 ± 0.3	380 ± 28	17.6 ± 3.2
0	30	1.5	12.2 ± 0.5	12.1 ± 0.5	11.7 ± 0.9	105 ± 8	12.5 ± 0.3	333 ± 18	11.8 ± 3.4
10	20	1.5	15.8 ± 0.3	14.1 ± 0.5	12.3 ± 0.5	113 ± 7	14.7 ± 0.5	339 ± 26	15.5 ± 3.8

^a σ_y is the stress at yield point.

^b σ_b is the stress at break point.

^c P.E.Y. is the percentage elongation at yield point.

^d P.E.B. is the percentage elongation at break point.

^e E is Young's modulus.

respectively. The peak values of $\tan \delta$ curves were recorded as transition temperatures. Each sample was analyzed at least in duplicate. Differential scanning calorimetry was performed on a Perkin–Elmer DSC-7, with temperature scanning from –55 to 160°C at 20°C/min.

2.6. Water absorption

To measure the water-soluble content in the soy protein sheet, a water absorption test was conducted following the ASTM D570-81 with minor modification. The samples dried at 50°C for 24 h were placed in distilled water at room temperature. After the sheet was removed from water, the container was placed in an oven at 50°C for 24 h to evaporate the water. The residuals were the water-soluble contents. The weight gain of the sheet plus the weight of the water-soluble residuals was counted as the total absorbed water. Three replicates of analysis were done for each sample.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Effects of plasticizers

3.1.1.1. Glycerol. Plasticizing effects of glycerol at various concentrations on mechanical properties of soy protein plastic sheets are shown in Table 1. The extrusion processing of soy protein sheets containing 10 parts of glycerol or less was very difficult, and the resulting sheets became very brittle after losing moisture. Sheets made with 10 parts of glycerol showed the highest tensile strength and Young's modulus, but the percentage elongation at break was only 3%. Sheets made with 20 parts of glycerol showed high toughness, strength, Young's modulus, and percentage elongation at yield point. The largest changes in strength, Young's modulus, and elongation at break were displayed between 20 and 30 parts of glycerol. A further increase in glycerol concentration above 30 parts resulted in large decreases in yield stress and yield elongation, but showed few changes in other mechanical properties. Elongation at break increased continuously with the increase of glycerol content.

Soy protein consists of polar and non-polar side chains. There are strong intra- and inter-molecular interactions, such as hydrogen bonding, dipole–dipole, charge–charge, and hydrophobic interactions. The strong charge and polar interactions between side chains of soy protein molecules restrict segment rotation and molecular mobility, which lead to increases in modulus, stiffness, yield point, and tensile strength. The charge and polar interactions between protein molecules also result in the brittleness of soy protein plastics. As a plasticizer, glycerol reduces the interaction between protein molecules and increases the flexibility, extensibility and processibility of soy protein plastics. The

Table 3

Effect of moisture content on mechanical properties of soy protein sheets (formulation: SPI 610 (100 parts), water (80 parts), glycerol (30 parts))

% RH ^a	Moisture (%)	σ_y^b (MPa)	σ_b^c (MPa)	P.E.Y. ^d (%)	P.E.B. ^e (%)	Strength (MPa)	E^f (MPa)	Toughness (MPa)
0	2.8	40.4 ± 2.0	38.1 ± 0.8	7.0 ± 0.2	13 ± 3	41.1 ± 1.5	1220 ± 32	4.2 ± 1.3
11	3.2	31.4 ± 1.4	24.6 ± 0.8	6.9 ± 0.3	77 ± 14	31.2 ± 1.4	1002 ± 66	19.7 ± 3.5
32	4.2	22.4 ± 0.8	18.9 ± 0.6	7.4 ± 0.2	95 ± 8	22.4 ± 0.8	735 ± 31	18.3 ± 1.7
50	7.7	8.4 ± 0.4	8.8 ± 0.4	9.6 ± 0.2	112 ± 3	8.9 ± 0.4	249 ± 35	9.4 ± 0.5
75	13.9	3.5 ± 0.1	4.1 ± 1.0	15.0 ± 1.7	159 ± 1	4.7 ± 0.3	70 ± 4	6.4 ± 0.5
93	26.0	1.2 ± 0.1	2.3 ± 0.1	14.4 ± 2.4	128 ± 11	2.4 ± 0.1	17 ± 1	2.4 ± 0.2

^a Samples were equilibrated for 1 week at different water activities.^b σ_y is the stress at yield point.^c σ_b is the stress at break point.^d P.E.Y. is the percentage elongation at yield point.^e P.E.B. is the percentage elongation at break point.^f E is Young's modulus.

T_g of soy protein decreased with the increase of glycerol concentration. High glycerol concentration also helped to retain moisture in the sheets, which further decreased the T_g . The remnant moisture contents were found to increase from 3.9% for the sheet with 20 parts of glycerol to 9.6% for the sheet with 50 parts of glycerol. The modulus of soy protein sheets was greatly changed by adjusting the glycerol level; therefore, soy protein sheets ranging from rigid to semirigid were obtained. For the sheets containing 10 and 20 parts of glycerol, the high Young's moduli indicated that soy protein sheets behaved like rigid plastics, and the yield stress of sheets containing 10 parts of glycerol was close to that of glassy polymers [12]. When the glycerol content increased to 30 parts, both Young's modulus and yield stress of soy protein sheets decreased significantly, indicating the soy plastics were greatly softened and became semi-rigid. The drastic decrease in yield stress with the increase of glycerol to 40 and 50 parts could be attributed to heterogeneous systems with high glycerol contents.

3.1.1.2. Methyl glucoside. Because the T_g of simple sugar is substantially higher than that of glycerol, using sugars as plasticizers can produce soy plastics with higher T_g and rigidity. For example, the T_g of glucose and sucrose are 38 and 78°C, respectively, compared with that of glycerol at -93°C [13]. In this study, methyl glucoside was used as a plasticizer to partially replace glycerol, and rigid sheets were produced. The results are shown in Table 2. When glycerol was partially replaced with 10 parts of methyl glucoside, tensile strength and toughness increased up to 24.4 and 33.3%, respectively. However, glycerol was still necessary in order to maintain a good processibility.

3.1.1.3. Moisture content. In addition to its crucial role in the gelation of soy protein and processing of soy protein resins, the moisture content in products greatly affected the properties of soy protein plastics as shown in Table 3. With the increase in moisture content, both tensile strength and modulus of the sheet specimens decreased rapidly,

whereas the elongation greatly increased. At 2.8% moisture content (equilibrated at 0% RH, TGA data), the soy protein sheet had the highest tensile strength and Young's modulus, but was very brittle. The high moduli at low moisture (2.8 and 3.2%) indicated that the soy protein sheets behaved like rigid plastics. The elongation greatly increased with the increase in moisture content, whereas mechanical strength and modulus continuously decreased. The toughness of the soy protein sheet passed through a maximum at 3.2 and 4.2% moisture (equilibrated at 11 and 32% RH, respectively). At 26% moisture level (equilibrated at 93% RH), the sheet lost most of its tensile strength and rigidity. Comparing the data in Tables 1 and 3, the results indicated that moisture affected the mechanical properties more effectively than glycerol. The results also indicated that soy protein-based sheets were very sensitive to the RH of the surrounding environment. With moisture content varying from 2.8 to 26%, the mechanical properties of soy protein sheets changed from those of rigid to semi rigid to soft plastics. Results of thermal analysis of these sheets are shown in Figs. 1 and 2.

3.1.2. Effects of cross-linking agents

To improve the rigidity of the sheets, ZnSO₄ was used to introduce chelating cross-links, and epichlorohydrin and glutaric dialdehyde were used for covalent cross-links between soy protein molecules. Both epichlorohydrin and glutaric dialdehyde can form covalent bonds with amino and hydroxyl groups of soy protein. Results of cross-linking effects are shown in Tables 4–6. The Young's modulus of the soy protein plastic sheet was significantly increased (29–51%) with the addition of ZnSO₄, whereas the strength, percentage elongation, and stress at yield were not significantly changed except when 2% of ZnSO₄ was added (Table 4). In addition to forming ionic bonds with functional groups (such as glutamic and aspartic acids), Zn²⁺ can form chelating complexes with oxygen, nitrogen, and sulfur

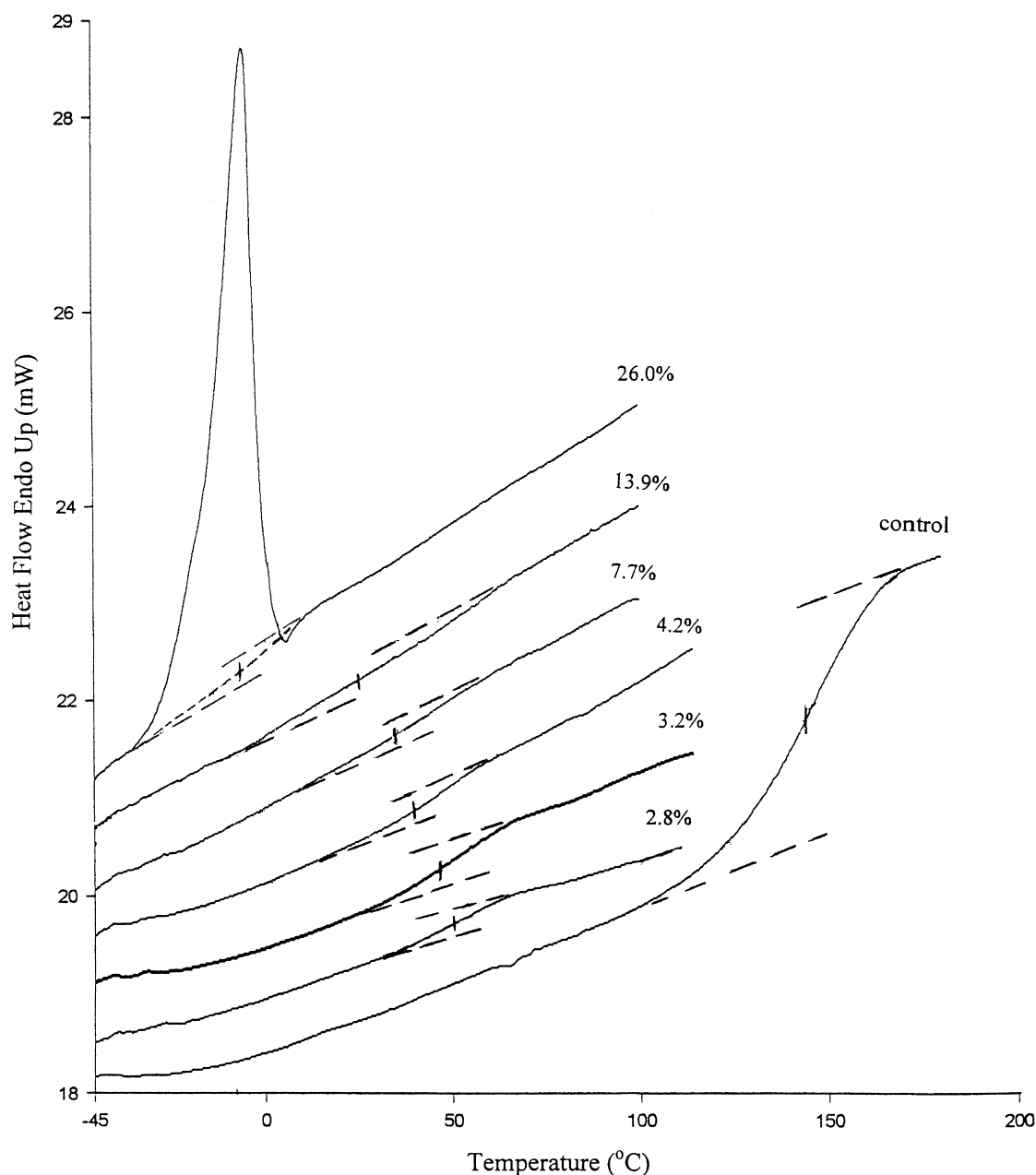


Fig. 1. DSC thermograms of soy protein sheets at different moisture contents. The sheets contained 30 parts of glycerol per 100 parts of soy protein. Heating rate = 20°C/min. The control was made by compression-molding and contained ca 0.5% moisture without glycerol.

containing groups of soy protein [14,15]. These interactions stiffened the soy protein molecules, and consequently, led to increases in Young's modulus. Results showed that cross-linking using epichlorohydrin and glutaric dialdehyde was more effective in increasing the rigidity (higher Young's modulus) of soy protein plastic sheets than using ZnSO_4 (Table 4–6). However, the processibility became very poor when soy protein contained 0.4% epichlorohydrin or glutaric dialdehyde. The resin with 1.5% ZnSO_4 still retained good processibility, indicating that the cross-linking by Zn^{2+} was labile [14] at an elevated temperature.

3.2. Thermal and dynamic mechanical properties

3.2.1. DSC analysis

Fig. 1 shows the DSC thermograms of soy protein sheets with different moisture contents. The soy protein sheet samples used in this study were the same as those in Table 3. Because glycerol (30 parts) was included in the sheet formulation to facilitate extrusion processing and to improve mechanical properties of the products, the soy protein sheet was plasticized with or without additional moisture. With the increase in moisture content, the glass transition temperature (T_g) of the protein sheet changed to

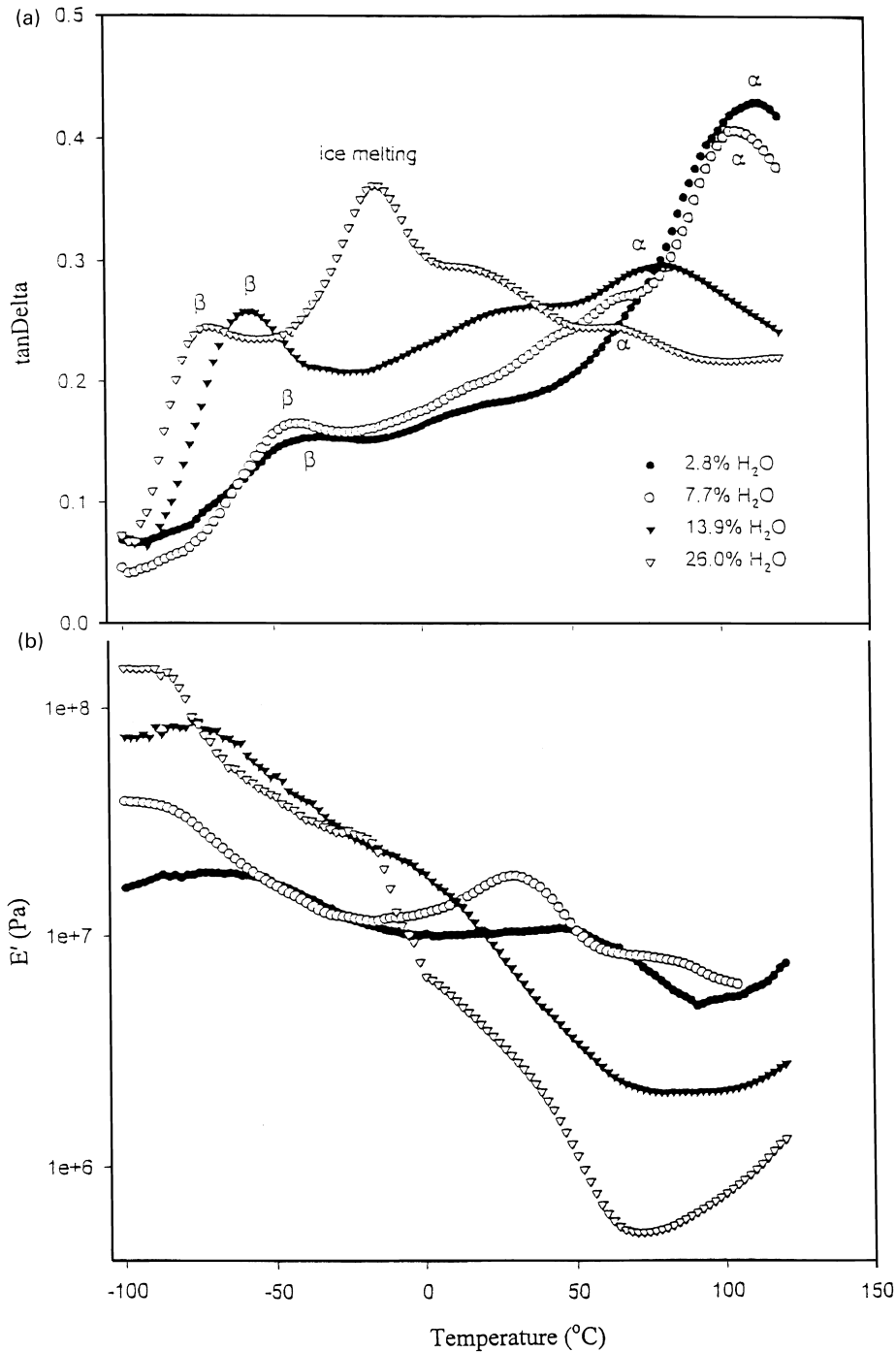


Fig. 2. Variation of $\tan \delta$ (a) and E' (b) of soy protein sheets with temperature at different moisture contents. The sheets contained 30 parts of glycerol per 100 parts of dry soy protein. The temperature scan was from -100 to 130°C at $2^\circ\text{C}/\text{min}$, and the frequency of the dynamic force was 1 Hz.

significantly lower temperatures, reflecting the plasticizing effect of water. Unlike the intact soy protein that has the characteristic of two glass transitions for 11S and 7S fractions [10], the DSC of soy protein sheets showed a single T_g , indicating complete denaturation of soy protein during the sheet processing. A soy protein plastic sample made by compression-molding, containing ca 0.5% moisture and

no glycerol, was used as an unplasticized control in this study. The control soy protein plastic showed a sharp glass transition, with a T_g at ca. 145°C . This result agreed with that (150°C) reported by Sue et al using DMA analysis [7]. With glycerol and water, the plasticized protein sheets showed decreased T_g . The T_g decreased continuously with an increase in moisture content. When the moisture content

Table 4

Effect of zinc sulfate on mechanical properties of soy protein sheets (formulation: SPI 760 (100 parts), water (80 parts), glycerol (30 parts))

ZnSO ₄ (parts)	σ_y^a (MPa)	σ_b^b (MPa)	P.E.Y. ^c (%)	P.E.B. ^d (%)	Strength (MPa)	E^e (MPa)	Toughness (MPa)
0	12.6 ± 0.2	14.1 ± 0.4	11.5 ± 0.4	119 ± 12	14.3 ± 0.5	257 ± 24	16.0 ± 1.9
0.5	13.7 ± 0.4	13.4 ± .5	10.4 ± 0.8	101 ± 3	13.7 ± 0.4	332 ± 10	12.7 ± 0.9
1.0	13.8 ± 0.6	14.8 ± 0.4	11.8 ± 0.4	144 ± 20	14.8 ± 0.4	381 ± 45	19.2 ± 2.5
1.5	13.0 ± 0.9	14.9 ± 1.0	12.0 ± 1.5	148 ± 15	14.9 ± 0.9	348 ± 33	19.4 ± 1.5
2.0	16.5 ± 1.2	16.7 ± 0.8	10.3 ± 0.7	131 ± 14	16.7 ± 0.8	389 ± 11	21.7 ± 3.9

^a σ_y is the stress at yield point.^b σ_b is the stress at break point.^c P.E.Y. is the percentage elongation at yield point.^d P.E.B. is the percentage elongation at break point.^e E is Young's modulus.

was low, even with 30 parts of glycerol, the T_g of soy protein sheet was above room temperature. This resulted in relatively high yield stresses and moduli for those samples at room temperature (Table 3).

DSC thermogram of soy protein sheets containing 26% moisture showed a peak at about -18°C (onset temperature) (Fig. 1), indicating the existence of crystallizable (or freezable) water (mixed with glycerol in this case), and the T_g of soy protein sheets (ca. -7°C) was masked by this peak. This result agreed with that reported by Ponomariova and co-workers [16,17] who studied the function of water in a hydrophilic polymer–water system, such as poly(vinyl alcohol) and polyacrylamide. They concluded that when the water content was above the critical concentration (c^*) where it began to crystallize upon cooling, the T_g did not decrease according to the Fox equation but remained constant and merged with the crystallization or ice melting peak. The very low Young's modulus of the soy protein sheet containing 26% moisture also indicated that this sheet was in a rubbery state at room temperature (Table 3). In this study, the soy protein sheets showed T_g values varying from ca. 50 to -7°C with 30 parts of glycerol and moisture ranging from 2.8 to 26%.

3.2.2. Damping spectra

Fig. 2 shows the DMA spectra of soy protein sheets with

30 parts of glycerol and different moisture contents. The transitions that occurred in the low temperature range were attributed to β -transitions. Because these transitions varied substantially with moisture content and thermal expansion, they were likely motions of the hydrated soy protein side groups, which depended on moisture content [18] and/or the crankshaft motion of the main chains. These sheets showed the temperature of β -transition varying from -72 to -33°C with moisture ranging from 26.0 to 2.8% (Fig. 2a).

The α -transition fell into a broad range depending on the moisture content. For the sheet with 26% moisture, the $\tan \delta$ curve showed a major peak at ca. -15°C , which corresponded with the melting of the freezable water (mixed with glycerol) revealed by DSC. The α -transition temperatures of the samples were much higher than the T_g values determined by using the midpoint of the change in heat capacity measured by DSC (Fig. 1). This was attributed to the continuous loss of moisture as the temperature increased during DMA scanning. To confirm this observation, sheet samples with 26% moisture were scanned from -115°C to 40, 60, 80 and 100°C and the weight losses at each of above temperatures were found to be 8.8, 9.4, 15.5 and 22.7%, respectively. Additionally, both the α - and β -transitions were shifted to higher temperatures in subsequent rescans (data not shown). Although the slow vaporization of

Table 5

Effect of epichlorohydrin as cross-linking agent on mechanical properties of soy protein sheets (formulation: SPI 760 (100 parts), water (80 parts), glycerol (30 parts))

ECH ^a (parts)	σ_y^b (MPa)	σ_b^c (MPa)	P.E.Y. ^d (%)	P.E.B. ^e (%)	Strength (MPa)	E^f (MPa)	Toughness (MPa)	Water absorption %, 2 h
0	12.6 ± 0.2	14.1 ± 0.4	11.5 ± 0.4	119 ± 12	14.3 ± 0.5	257 ± 24	16.0 ± 1.9	92 ± 2
0.1	13.3 ± 0.2	15.7 ± 1.0	10.9 ± 0.3	107 ± 12	16.9 ± 0.7	516 ± 45	18.6 ± 3.1	110 ± 4
0.2	15.5 ± 0.9	16.3 ± 0.9	10.3 ± 1.4	162 ± 19	16.5 ± 0.7	533 ± 42	21.5 ± 2.2	102 ± 17
0.4	18.0 ± 1.2	16.9 ± 0.3	10.5 ± 1.0	162 ± 15	16.9 ± 0.9	586 ± 46	24.9 ± 2.0	102 ± 9

^a ECH = epichlorohydrin.^b σ_y is the stress at yield point.^c σ_b is the stress at break point.^d P.E.Y. is the percentage elongation at yield point.^e P.E.B. is the percentage elongation at break point.^f E is Young's modulus.

Table 6

Effect of glutaric dialdehyde as cross-linking agent on mechanical properties of soy protein sheets (formulation: SPI 760 (100 parts), water (80 parts), glycerol (30 parts))

Glutaric dialdehyde (parts)	σ_y^a (MPa)	σ_b^b (MPa)	P.E.Y. ^c (%)	P.E.B. ^d (%)	Strength (MPa)	E^e (MPa)	Toughness (MPa)	Water absorption %, 2 h
0	12.6 ± 0.2	14.1 ± 0.4	11.5 ± 0.4	119 ± 12	14.3 ± 0.5	257 ± 24	16.0 ± 1.9	92 ± 2
0.1	17.0 ± 0.5	15.5 ± 1.1	10.0 ± 0.6	131 ± 21	16.3 ± 0.5	450 ± 82	19.7 ± 3.6	106 ± 7
0.2	16.2 ± 0.6	16.2 ± 0.4	10.5 ± 0.3	148 ± 16	16.3 ± 0.4	550 ± 80	22.2 ± 2.5	107 ± 8
0.4	16.9 ± 7.8	16.5 ± 1.0	9.4 ± 0.4	137 ± 24	17.3 ± 0.6	545 ± 45	21.0 ± 4.1	109 ± 6
0.6	15.3 ± 0.8	15.6 ± 0.9	10.8 ± 0.5	146 ± 8	15.8 ± 1.2	494 ± 55	21.0 ± 1.6	90 ± 3

^a σ_y is the stress at yield point.

^b σ_b is the stress at break point.

^c P.E.Y. is the percentage elongation at yield point.

^d P.E.B. is the percentage elongation at break point.

^e E is Young's modulus.

glycerol and other volatile components in soy protein could also contribute to the total weight loss, the major weight loss was attributed to water. A similar observation was reported for glass transition of gluten by Kalichevsky et al. [13]. In their study, the authors studied the phenomena of moisture loss during the DMA scan and found that a loss of 1% in the water content during scanning resulted in a 5°C upward shift in the $\tan \delta$ peak temperature. In our study, the α -transition temperatures of sheets containing 7.7 and 2.8% moisture were above 100°C and were quite close to each other. Two explanations could account for this phenomenon. First, because samples were scanned in an oven in a DMA instead of sealed pans (in DSC), the loss of moisture during the scan resulted in changes of α -transitions to higher temperatures. Second, there was glycerol (30 parts) in the soy protein formulation, and the plasticizing effect of glycerol made the effect of moisture at low contents less significant.

On the basis of the above observations, the T_g values obtained by DSC were more accurate and reliable for soy protein plastics containing moisture. The T_g values from the $\tan \delta$ peaks, on the other hand, tend to be substantially higher.

3.2.3. Dynamic modulus

Similar to what was reported by Cocero and Kokini for glutenin [19], the drop in storage modulus (E') of soy plastic sheets at T_g was not catastrophic as in the case of synthetic polymers (usually more than 3 orders of magnitude). The E' values of samples with low moisture content (2.8 and 7.7% H₂O) showed the least temperature dependence in the whole temperature range (Fig. 2b). On the other hand, the E' values of samples containing high moisture (26 and 13.9% H₂O) greatly decreased with the increase in temperature. Furthermore, E' of the sheets containing 2.8 and 7.7% moisture gradually decreased with the increase in temperature, reaching a minimum at ca. 5 and -16°C, respectively. E' then showed an obvious recovery (seen as a bump in the curve) with further increase in temperature, especially for the sheet with 7.7% moisture. This behavior was similar to that of rat-tail tendons and plasticized collagen membranes reported by

Chien and Chang [20]. According to those authors, the minimum E' was attributed to the devitrification of water bound to the protein. After devitrification, the recovery of mechanical strength was obvious for sheets that contained relatively low moisture, but not for the sheets with excess moisture. The recovery of mechanical strength was attributed to the increased interactions between protein molecules resulting from the loss of water. For samples with excess moisture content, however, the mechanical strength was significantly reduced because of the plasticizing effect of moisture that remained in the samples.

In the sub-ambient temperature, the E' of soy protein sheets increased with the increase in moisture content. This could be attributed to the antiplasticization effect at the very low temperature [7]. At this low temperature, the water-glycerol mixture crystallizes [21]. Therefore, the plasticizers, water and glycerol, stiffened the soy protein plastics instead of softening them. A similar phenomenon was reported for nylon 6 and poly(L-leucine-co-glutamic acid) [22].

3.3. Water absorption

Fig. 3 shows the water absorption of soy protein sheets after different immersion times. The water absorption of the soy protein sheet after 20 h immersion was up to ca. 180%, and most of the water uptake occurred in the first few hours. With the presence of two parts of ZnSO₄, the water absorption of soy protein sheets was significantly reduced (ca. 30%). There was no clear relationship between water absorption and the concentration of cross-linking reagents (epichlorohydrin and glutaric dialdehyde) present in the soy protein sheets, as shown in Tables 5 and 6. This could be attributed to the fact that cross-linking did not change the hydrophilic nature of soy protein. In addition, at such low concentrations of cross-linking agents, degrees of cross-linking were not sufficient to reduce the swelling and water uptake during immersion. Thus, it was demonstrated that covalent cross-linking reactions were not effective in reducing water absorption of soy protein plastics.

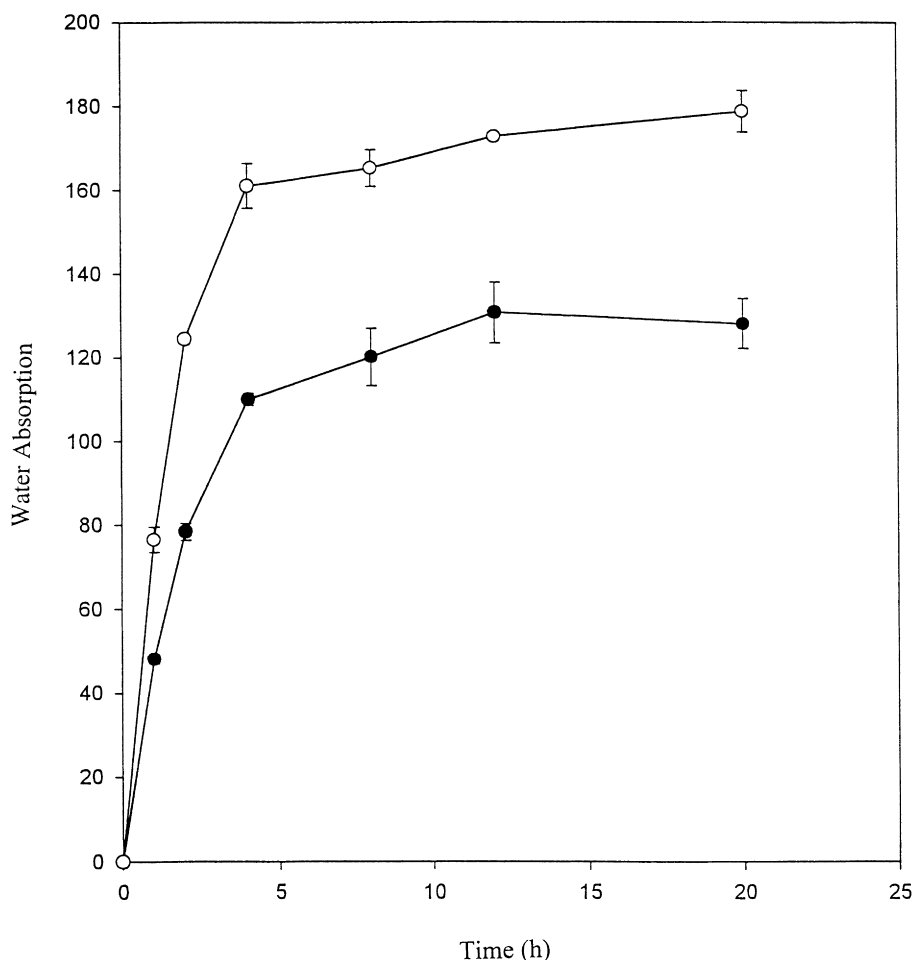


Fig. 3. Water absorption of soy protein sheets as a function of time. O: Sheets contained 30 parts of glycerol per 100 parts of soy protein; ●: sheets contained 30 parts of glycerol and two parts of $ZnSO_4$ per 100 parts of soy protein.

4. Conclusions

The soy protein sheet was usually in its glassy state and showed relatively high strength and modulus unless it contained high moisture and glycerol as plasticizers. Methyl glucoside could be used to partially replace glycerol for making rigid sheets. Zinc sulfate, epichlorohydrin, and glutaric dialdehyde all increased rigidity and other mechanical properties of the soy protein sheets through cross-linking, but they also led to poor processibility at high concentrations. The dynamic mechanical behavior of soy protein plastics was complicated because of the loss of water during DMA scanning at different temperatures. Thus, glass transition temperatures of soy protein sheets with different moisture contents determined by using DSC were more reliable than that obtained by using DMA. At very low temperatures ($< -50^\circ C$), water and glycerol showed an antiplasticization effect. Cross-linking of soy protein sheets by using covalent cross-linking reagents did not reduce the water absorption of the plastics.

Acknowledgements

The authors gratefully acknowledge financial support from the Iowa Soybean Promotion Board.

References

- [1] Welsby D, Kolar C, Richert S. *Inform* 1998;9:250.
- [2] Brother GH, Mckinney LL. *Ind Eng Chem* 1939;30:84.
- [3] Brother GH, Mckinney LL. *Ind Eng Chem* 1940;32:1002.
- [4] Paetau I, Chen C, Jane J. *Ind Eng Chem Res* 1994;33:1821.
- [5] Paetau I, Chen C, Jane J. *J Environ Polym Degrad* 1994;2:211.
- [6] Spence K, Allen AL, Wang S, Jane J. In: Ottenbrite R, Huang S, Park K, editors. *Hydrogels and biodegradable polymers for bioapplications*. Washington, DC: ACS, 1996. p. 149.
- [7] Sue H, Wang S, Jane J. *Polymer* 1996;38:5035.
- [8] Wang S, Sue H, Jane J. *J Macromol Sci-Chem A* 1996;33(5):557.
- [9] Otaigbe J, Adams D. *J Environ Polym Degrad* 1997;5:199.
- [10] Morales A, Kokini JL. *Biotechnol Prog* 1997;13:624.
- [11] Kalichevsky M, Jaroszkiewicz E, Blenshard J. *Int J. Biol Macromol* 1992;14:267.
- [12] Miller E. *Properties modification in engineering plastics*. Engineered

- materials handbook, vol. 2. Metal Park, OH: ASM International, 1988. p. 493–507.
- [13] Kalichevsky M, Jaroszkiewicz E, Blenshard J, *Int J. Biol Macromol* 1992;14:257.
- [14] Katz AK, Glusker J, Beebe S, Bock C. *J Am Chem Soc* 1996;118:5752.
- [15] Berg J, Shi Y. *Science* 1996;271:1081.
- [16] Ponomariova T, Melnichenko Y, Albouy PA, Rault J. *Polymer* 1997;38:3561.
- [17] Rault J, Graff R, Ping ZH, Nguyen QT, Neel J. *Polymer* 1995;36:1655.
- [18] Baschek G, Hartwig G, Zahradnik F. *Polymer* 1999;40:3433.
- [19] Cocero AM, Kokini JL. *J Rheol* 1991;35:257.
- [20] Chien JCW, Chang EP. *Biopolymers* 1972;11:2015.
- [21] Green JL, Fan J, Angell CA. *J Phys Chem* 1994;98:13 780.
- [22] Hiltner A, Anderson JM, Baer E. *J Macromol Sci-Phys B* 1973;8(3–4):431.