

Thermal and Mechanical Properties and Water Absorption of Sodium Dodecyl Sulfate-Modified Soy Protein (11S)

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ABSTRACT: The thermal and mechanical properties and water absorption of sodium dodecyl sulfate (SDS)-modified 11S soy protein and molded plastics made from it were studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), mechanical tests, and scanning electron microscopy (SEM). The DSC results showed that both the temperature and enthalpy of thermal denaturation of modified 11S solutions decreased as the SDS concentration increased. Nonfreezing water of the modified 11S solution had a minimum value at 1.0% SDS. The ordered structure of SDS-modified 11S protein was recovered and/or newly formed during the freeze-drying process. Both DSC and DMA results showed that SDS was a plasticizer of 11S, and the glass transition temperature of modified 11S plastics decreased with increasing SDS concentration. Both the tensile strength and elongation of modified 11S plastics first decreased and then increased as the SDS concentration increased, and 5.0% SDS-modified 11S plastic had the highest tensile strength and elongation. The SEM observations supported these results. A water-absorption test showed a reduction in the water resistance of 11S plastics after SDS modification. The rate of water absorption increased with increasing SDS concentration. The hydrophobic interaction between SDS molecules and 11S protein was found to have important effects on the thermal and mechanical properties and the water absorption of 11S plastics. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 166–175, 2001

Key words: 11S soy protein; sodium dodecyl sulfate; thermal properties; mechanical properties; water absorption

INTRODUCTION

With the wide use of synthetic petroleum polymer materials, the environmental impact of wastes from disposable plastic items has risen and become more acute worldwide in recent years. Over 21.9 billion pounds of plastic materials were discarded in the United States in 1992, and this

figure was expected to reach 34.2 billion pounds by 2002.¹ The development of biodegradable plastics, which degrade in the environment by means of humidity and the action of microorganisms, therefore is needed urgently to help solve these environmental problems. The loss of landfill space and a change in the public perceptions of acceptable waste, waste reduction, and waste elimination have increased interest in biodegradable plastics.

Soybean protein, as a degradable biopolymer, has been considered recently as an alternative to petroleum polymer in the manufacture of adhesives, plastics, and various binders. Soybean protein, the major component of the soybean (30–

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45%),² is readily available from renewable resources and agricultural processing by-products. Plastics made from soy protein have high strength, for example, 40 MPa of tensile strength for plastics made from soy protein powder with 11.7% moisture content,³ and good biodegradable performance.

Much research on soybean plastics was conducted in the 1930s and 1940s, and soybean products were incorporated into phenolic resins mainly as fillers or extenders to decrease the cost of the plastic.^{4,5} However, from then on, little work has been done to research and develop soy protein plastics, because petroleum-based plastics with their lower price and better performance dominated the market. In the 1990s, soy protein plastics gained researchers' attention again for their environmentally friendly properties. Most studies were focused on the mechanical properties and water absorption of soy protein plastics and showed that both were affected greatly by the composition of the protein and the processing conditions.^{3,6-8} Soy protein plastics are rigid, brittle, and water-sensitive. Therefore, many efforts have been made to modify their brittleness and to improve their water resistance. Incorporation of plasticizers, such as glycerol⁹⁻¹¹ and polyols,^{12,13} into soy protein plastics was a popular method to improve processability and toughness. Polysaccharides also were added to improve the properties of soy protein materials.^{14,15} Starch is a polymeric material that was used widely to modify soy protein plastics.¹⁶⁻²⁴ These soy protein-starch plastics could be extruded and injection-molded into articles of various shapes and sizes, and the products had good tensile properties and water resistance. Soy protein plastics treated with a crosslinking agent or incorporated with a cellulose filler also showed decreased water absorption.²⁵ Recently, blending with bioabsorbable polyphosphate fillers was found to improve significantly the intrinsic poor water resistance of biodegradable soy protein plastic.^{20,21,26,27} All these studies showed that soy protein plastics have great potential for practical use.

The goal of this study was to investigate the thermal and mechanical properties and water absorption of sodium dodecyl sulfate (SDS)-modified 11S soy protein and molded plastics made from it. Soy proteins contain two major components: glycinins (11S-rich globulin, 52%) and conglycinins (7S-rich globulin, 35%). We chose the 11S component to reduce the factors that potentially can affect the properties of the products. As a deter-

gent that can bind strongly with the protein molecule, SDS is able to produce a drastic cooperative conformation change of protein at low concentrations.²⁸ The interaction was mainly a hydrophobic interaction between the hydrophobic side chains of protein and the hydrophobic moieties of SDS.²⁸ Therefore, after SDS modification, the 11S protein was expected to have a different structure/conformation that would affect its properties greatly.

EXPERIMENTAL

Materials and Sample Preparation

Soybean protein fraction 11S was extracted from defatted soybean flour (Cargill, Cedar Rapids, IA) following the procedures described by Sun et al.²⁹ The 11S fraction had a purity of 90% and a moisture content of about 6 wt % as measured by an air-oven method.³⁰ The SDS (95%) was purchased from the Sigma Chemical Co. (St. Louis, MO).

To prepare SDS-modified 11S, 25 g of 11S protein was dissolved in a 200 mL solution with SDS concentrations of 0.5, 1.0, 2.0, and 5.0 wt %. The control sample was prepared by dissolving 25 g of 11S in 200 mL distilled water. The mixtures were stirred continuously for 6 h and then freeze-dried at -40°C and 10 Pa. The freeze-dried mixtures were powdered and contained approximately 8% moisture.

To prepare specimens for the tensile test, the control and SDS-modified 11S powders were placed in dumbbell-shaped tensile bar molds (type IV) and compression-molded using a Carver hot press (Model 3890 Auto "M," Carver Inc., Wabash, IN) according to ASTM standard D686-92.³¹ The specimens were molded at 140°C for 5 min and then cooled to 50°C before removal from the mold. Flash was removed carefully by sanding the edges of the specimens with 180-grade abrasive sandpaper. The moisture content of these specimens was about 3%.

Thermal Analysis

The thermal properties of the SDS-modified 11S solution, the SDS-modified 11S powder, and the molded SDS-modified 11S plastics were measured using a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC; Perkin-Elmer, Norwalk, CT). The instrument was calibrated with indium and zinc standards before official measurements,

and all measurements were conducted under a nitrogen atmosphere. All samples were quenched to -50°C and held at that temperature for 1 min. Then, the samples were scanned at $10^{\circ}\text{C}/\text{min}$ and quenched again to -50°C , held there for 1 min, and reheated at $10^{\circ}\text{C}/\text{min}$.

Nonfreezing water was determined using the DSC data following the method described by Ross.³² The same calorimetric measurements were carried out for pure water. From the ice-melting enthalpy of the sample, the globe water content of the sample, and the melting enthalpy of pure water, the nonfreezing water was calculated.

Dynamic Mechanical Analysis (DMA)

DMA was carried out using a DMA-7e dynamic mechanical analyzer (Perkin-Elmer) with the 3-point bending-rectangle method at 1 Hz. The heating rate was $3^{\circ}\text{C}/\text{min}$. The samples for DMA testing were cut from the narrow part of each molded bar and were about $15 \times 6 \times 2 \text{ mm}^3$.

Mechanical Property Tests and Morphology

Mechanical properties were measured using an Instron testing system (Model 4466, Canton, MA) according to ASTM standard D638-92.³³ Each specimen was preconditioned at 23°C and 50% relative humidity for 48 h and tested at a 5 mm/min crosshead speed. The stress, strain at maximum stress, and Young's modulus were obtained from the tests. The values presented are averages of five specimens. The fracture surface of tensile test specimens was observed using a scanning electron microscope (SEM; AutoScan, ETEC Corp., Highlands, TX) at an accelerated voltage of 20 kV. The specimens were coated with thin layers of gold of 200 Å before observation.

Water Absorption

Water absorption was measured using the ASTM standard D570-81.³⁴ The specimens were preconditioned by drying in an oven at 50°C for 24 h, then cooled in a desiccator for a few minutes, and weighed and submerged in distilled water at 25°C for various times. The specimens were removed from the water and dried with paper towels before weighing. Dry matter from the plastics left in the water during soaking also was included in the water-absorption calculation. The values presented are the averages of three specimens.

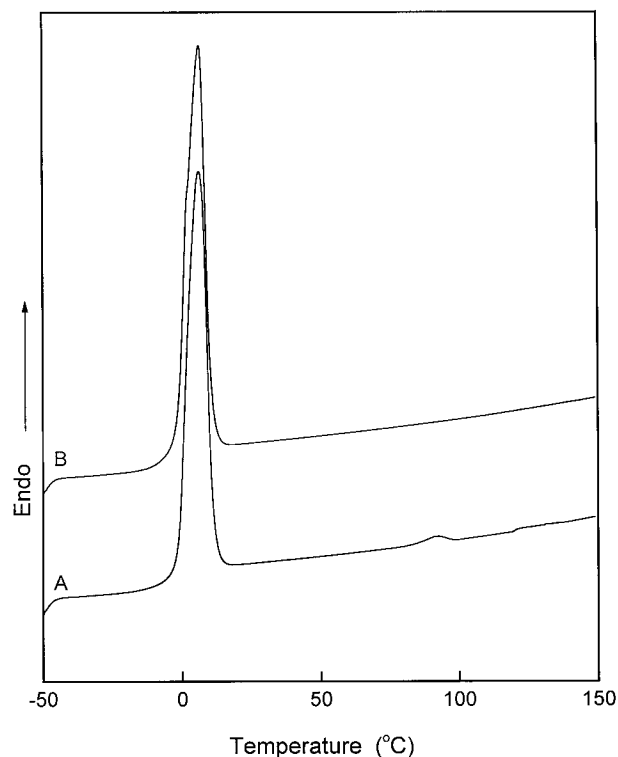


Figure 1 DSC thermograms of 0.5% SDS-modified 11S solution: (A) first scan; (B) second scan.

RESULTS AND DISCUSSION

Thermal Properties

11S Solution

Typical thermograms of an SDS-modified 11S solution showed an ice-melting transition at around 0°C and a thermal denaturation transition at around 90°C [Fig. 1(A)]. After solutions were heated to 150°C and then quenched, the thermograms, however, showed only the ice-melting transition [Fig. 1(B)], indicating that, under the experimental conditions, the thermal-unfolded 11S structure was not recovered after quenching. The 11S protein was denatured by the addition of SDS, and the thermal denaturation temperature (T_d) of the modified 11S protein decreased with increasing SDS concentration (Table I).

It is well known that SDS, as an anionic detergent, interacts quite well with protein to form complexes and induce conformational changes even at low concentrations.³⁵⁻³⁷ Its action at a low concentration was due to the existence of strong binding forces between SDS and protein molecules. Previous studies have indicated that this force is mainly a hydrophobic interaction, because

Table I Properties of Thermal Denaturation of 11S Solutions, 11S Powder, and Molded 11S Plastics as Affected by SDS Concentration

Treatment	11S Solution		11S Powder				Molded 11S Plastics	
	T_d (°C)	ΔH_d (J/g 11S)	T_{d1} (°C)	ΔH_{d1} (J/g 11S)	T_{d2} (°C)	ΔH_{d2} (J/g 11S)	T_d (°C)	ΔH_d (J/g 11S)
Control	95.6	20.3	—	—	166.4	19.8	161.8	11.2
0.5% SDS	92.6	10.4	—	—	164.6	21.1	163.9	13.7
1.0% SDS	91.6	7.8	—	—	162.6	18.7	161.4	11.0
2.0% SDS	89.2	5.8	75.6	1.8	158.4	14.1	157.9	7.1
5.0% SDS	85.0	2.4	84.8	7.2	148.4	10.2	—	—

even lower concentrations sufficed to induce denaturation when anionic detergents with more strongly hydrophobic side chains were used.^{28,36} In our experiments, the hydrophobic side chains of SDS interacted with the 11S protein molecules to form 11S–SDS complexes and, at the same time, led to denaturation of 11S. However, the formation of the complex might have made the ordered structure of 11S more labile to heat and, thus, resulted in the decrease of T_d with increasing SDS concentration. Because of the partial denaturation of 11S with the addition of SDS, the enthalpy of thermal denaturation (ΔH_d) decreased as the SDS concentration increased (Table I). However, even at 5.0% SDS, the thermograms still showed a thermal denaturation transition. In fact, Tanford²⁸ reported that protein was only partially unfolded after denaturation by detergents even at high concentrations and that existing ordered regions or newly formed ones or possibly even isolated hydrophobic side chains could interact with the hydrophobic moieties of detergent molecules to form micellelike regions.

Nonfreezing water (or bound water) reflects the interaction between protein and water molecules and relates closely to the water-holding capacity of protein. The study of nonfreezing water also can provide important information on the structure and functional properties of proteins.^{38–43} The nonfreezing water of the SDS-modified 11S solution was calculated from the ice-melting transition^{41–43} and plotted against the SDS concentration (Fig. 2). Nonfreezing water of the modified 11S solution both before and after thermal denaturation first decreased and then increased as the SDS concentration increased and reached a minimum value at about 1.0% SDS.

During modification, the exposure of hydrophobic groups, which were buried when 11S was in a folded state, would decrease the nonfreezing water. On the other hand, however, the interaction between the hydrophobic moieties of SDS and the hydrophobic side chains of 11S led to the formation of a micellelike region, which reduced the hydrophobicity of 11S. The binding of SDS detergent ions to 11S also increased the net charge of 11S. These two factors would increase the nonfreezing water. At low SDS concentrations, the effect of the exposure of hydrophobic groups was predominant, and, hence, the nonfreezing water decreased. At high SDS concentrations, the effect of the latter two factors (interaction and binding) was predominant, and, hence, the nonfreezing

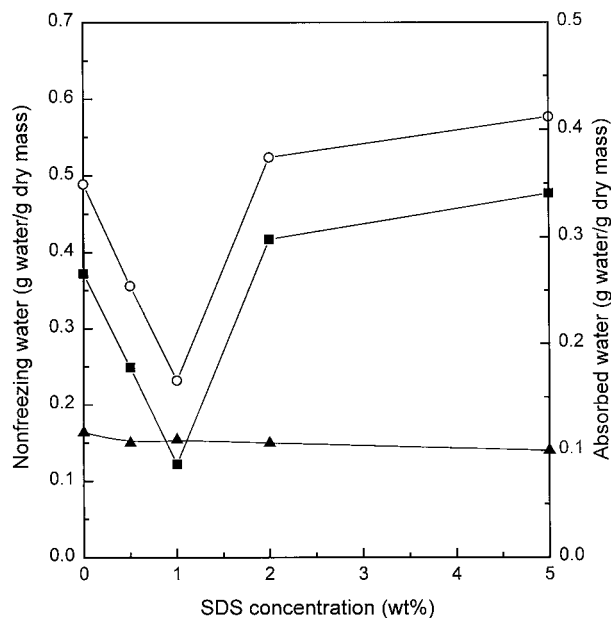

Figure 2 Nonfreezing water of 11S solutions (■) before and (○) after denaturation and (▲) absorbed water as affected by SDS concentration.

Table II Glass Transition Temperature (°C) of 11S Powder and Molded 11S Plastics as Affected by SDS Concentration

Treatment	11S Powder DSC Results	Molded 11S Plastics	
		DSC Results	DMA Results
Control	43.0	49.1	51.3
0.5% SDS	42.5	47.8	48.8
1.0% SDS	42.2	45.7	47.5
2.0% SDS	39.5	43.2	45.9
5.0% SDS	38.0	38.2	44.2

water increased. The nonfreezing water of 11S was always greater after thermal denaturation than before (Fig. 2). The absorbed water of the modified 11S solution during thermal denaturation also was calculated,⁴³ and it remained almost constant with variation of the SDS concentrations (Fig. 2). This was understandable because the absorbed water was determined mainly by exposure of hydrophilic groups to water during the thermal denaturation⁴³ and SDS interacted mainly with nonpolar groups of the 11S protein and had little effect on the exposure of polar groups during the thermal denaturation.

11S Powder

The 11S powder exhibited a glass transition temperature (T_g) in the temperature range of 43–38°C, which decreased with an increasing SDS concentration (Table II). The decrease of T_g apparently was due to plasticization of 11S protein by SDS. The DSC thermograms of both control and modified powders still showed thermal denaturation transitions, which decreased as SDS concentration increased (Fig. 3). Table I shows that the ΔH_d of the modified powder was larger than that of the corresponding modified solution. This suggested that the ordered structure of denatured 11S was partially recovered and/or reformed during the freeze-drying process. This reforming was confirmed further by the ΔH_d value of 0.5% SDS-modified powder, which was even larger than that of the control sample (Table I) and by the appearance of a new transition peak at about 80°C for the 11S powders modified with 2 and 5% SDS (Fig. 3 and Table I). The new endothermic transition peak was believed to be due to the destruction of the newly formed less-stable ordered structure of the 11S protein. Other studies have re-

ported that a low concentration of SDS was beneficial to the formation of an α -helix conformation.^{44–46} Thus, the interaction of SDS with the 11S protein molecule could have formed a new ordered structure during the process of freeze-drying. It was reported that the T_g value of 11S soy protein decreased from 160 to -17°C as the moisture content increased from 0 to 40%.⁴⁷ In our experiments, the moisture content of the SDS-modified solution was 85–90%. The T_g of the SDS-modified solutions should be much lower than the freeze-drying temperature (-38 to -40°C) although the T_g values of the solutions were not obtained due to the limit of the experimental conditions. Therefore, the protein molecules still had enough mobility to change their structure during the early stage of the freeze-drying. The second DSC scans of both the control and the modified 11S powders after they were heated to 200°C and then quenched still showed glass transitions but the thermal-denaturation transitions at both high and low temperatures had disappeared.

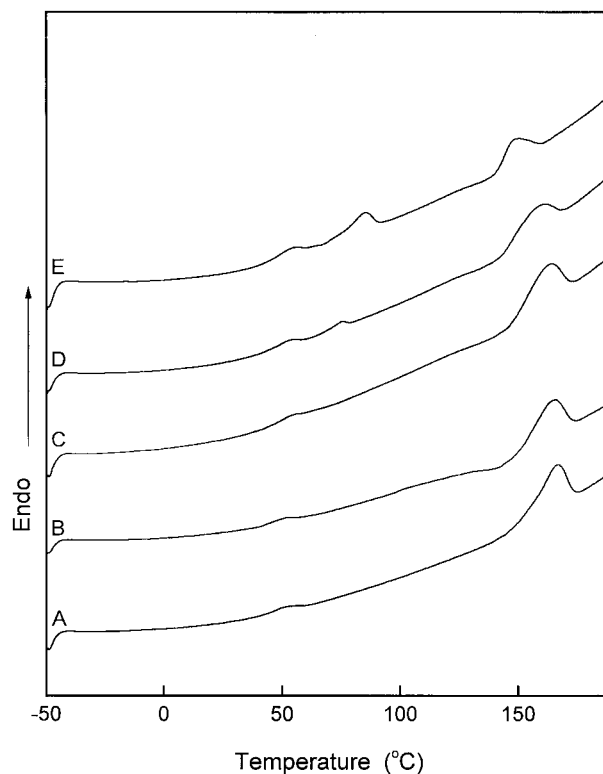


Figure 3 DSC thermograms of (A) 11S powder: control, (B) 0.5% SDS-modified, (C) 1.0% SDS-modified, (D) 2.0% SDS-modified, and (E) 5.0% SDS-modified.

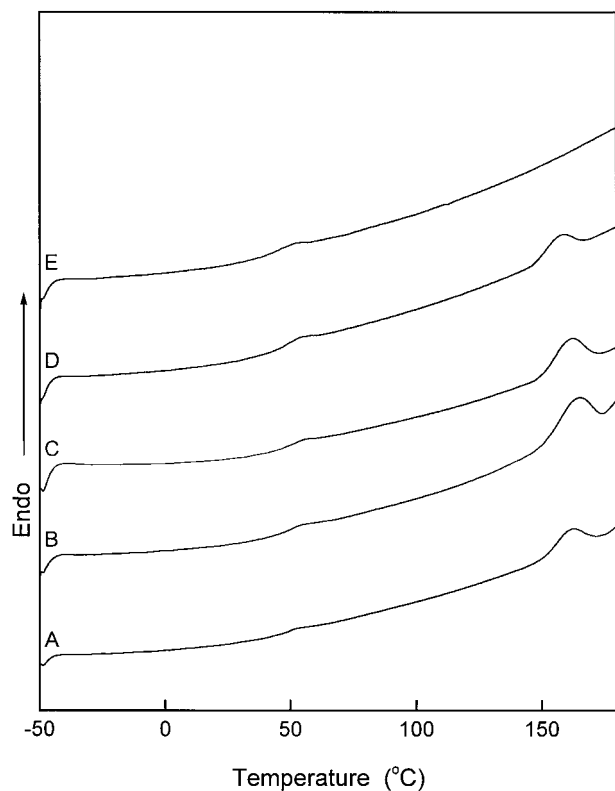


Figure 4 DSC thermograms of 11S plastics: (A) control; (B) 0.5% SDS-modified; (C) 10% SDS-modified; (D) 2.0% SDS-modified; (E) 5.0% SDS-modified.

Molded 11S Plastics

The molded plastics made from both control and SDS-modified 11S powders exhibited a T_g in the range of 50 to 38°C, which decreased with increasing SDS concentrations (Table II). This reduction also was attributed to the plasticization of 11S by SDS. Furthermore, the T_g of the molded plastics was larger than that of corresponding powders (Table II), because possible crosslinking reactions among sulfhydryl, amino, carboxyl, and hydroxyl groups during the hot-press process restricted the movement of the chain segment in the 11S plastics. The decrease of moisture content during molding would also increase the T_g 's (moisture content was about 8% for powder and 3% for plastics). However, loss of the plasticizer of SDS was less possible because of its high melting temperature (204–207°C).

The control and the low-concentration SDS-modified 11S plastics still showed a thermal denaturation transition. However, no thermal denaturation transition was observed for the 5.0% SDS-modified 11S plastics (Fig. 4). This was because the T_d of the 5.0% SDS-modified 11S powder was relatively low (Table I), and this sample was completely thermally denatured during the hot-press process. Note that both the T_d and ΔH_d of the modified plastics first increased and then decreased as the SDS concentrations increased (Table I). This trend probably was initiated by a

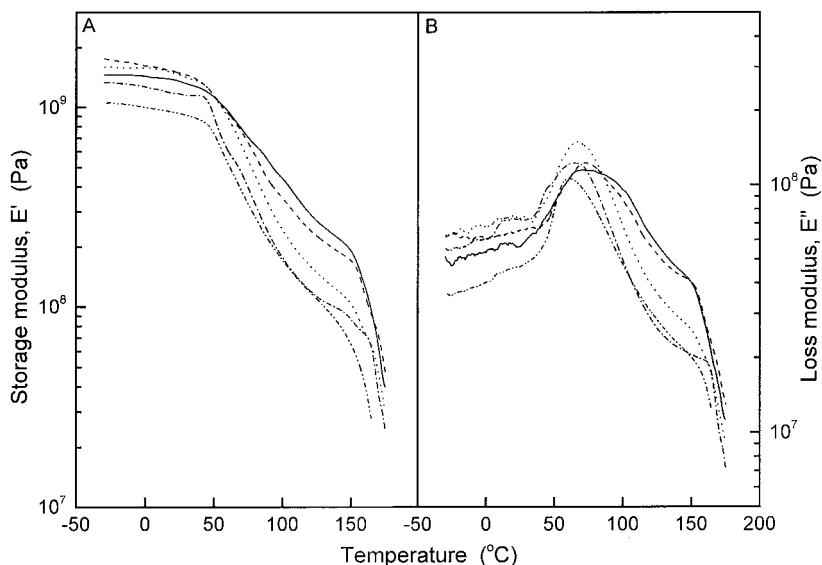


Figure 5 Dynamic mechanical properties, (A) storage modulus E' and (B) loss modulus E'' , of 11S plastics: (—) control; (---) 0.5% SDS-modified; (·····) 1.0% SDS-modified; (- · - · - ·) 2.0% SDS-modified; (- - - - -) 5.0% SDS-modified.

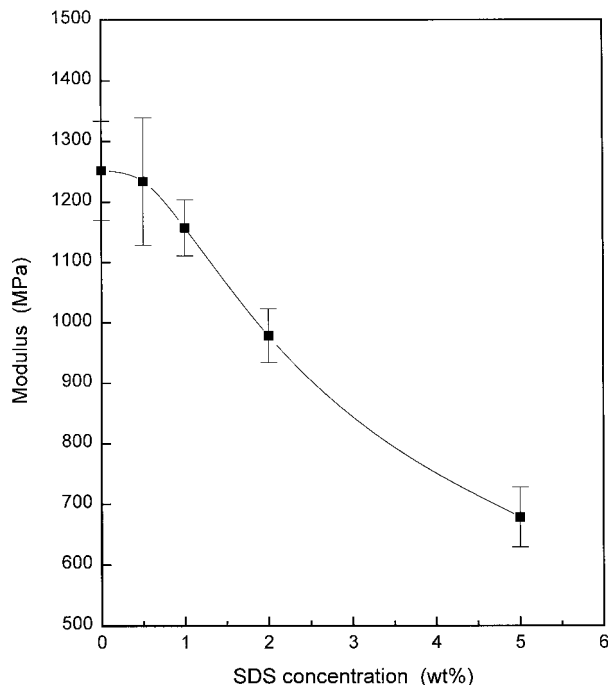


Figure 6 (■) Modulus of 11S plastics as affected by SDS concentration.

structure change during the hot-press process and indicated that the 0.5% SDS-modified plastic had a relatively high content of an ordered structure.

Dynamic Mechanical Properties of Molded 11S Plastics

Both the control and SDS-modified 11S plastics showed two sharp decreases for the storage modulus (E') [Fig. 5(A)]. The first one was due to the glass transition of 11S plastics. At the T_g , the mechanical energy absorbed by the 11S molecule reached its maximum value and, hence, showed a peak in the loss modulus (E'') curve [Fig. 5(B)]. The second decrease in the E' curve could be attributed to the denaturation transition and/or the entangled polymer flow of 11S plastics. In this study, the onset temperatures of the E' curve for both control and modified 11S were taken as the T_g , and the results are summarized in Table II. Similar to the T_g results from DSC, the T_g obtained from DMA also decreased with an increasing SDS concentration. Therefore, both the DSC and DMA results showed that SDS could be considered as a plasticizer for 11S.

Mechanical Properties and Morphology of Molded 11S Plastics

Without a plasticizer, 11S plastics are rigid and brittle. The control plastic had a Young's modulus (E) of 1.25 GPa, a stress at break (σ_B) of 24.5 MPa, and a strain at break (ϵ_B) of 2.02% under the experimental conditions (Figs. 6 and 7). After modification by SDS, E decreased with increasing SDS concentration because of the plasticization. However, σ_B and ϵ_B had minimum values at 0.5% SDS (Fig. 7). This phenomenon was contradictory to the plasticization effect and was explained as the following: In the native state, the 11S molecule has a globular, compact ordered structure. With SDS modification and thermal denaturation, however, 11S had a loose and disordered structure. This kind of structure improved interactions (both polar and nonpolar interactions) among 11S protein molecules, because they were brought closer together and the contact area among them was increased. These improved intermolecular interactions increased the σ_B and ϵ_B of the 11S plastics, and the 5.0% SDS-modified plastics had the highest σ_B (33.6 MPa) and ϵ_B (6.85%). However, as we have discussed, the 0.5% SDS-modified 11S plastic had a higher ΔH_d (Table I), indicating that it had a more ordered structure than the one with 5.0% SDS. Therefore, the intermolecular interactions in the

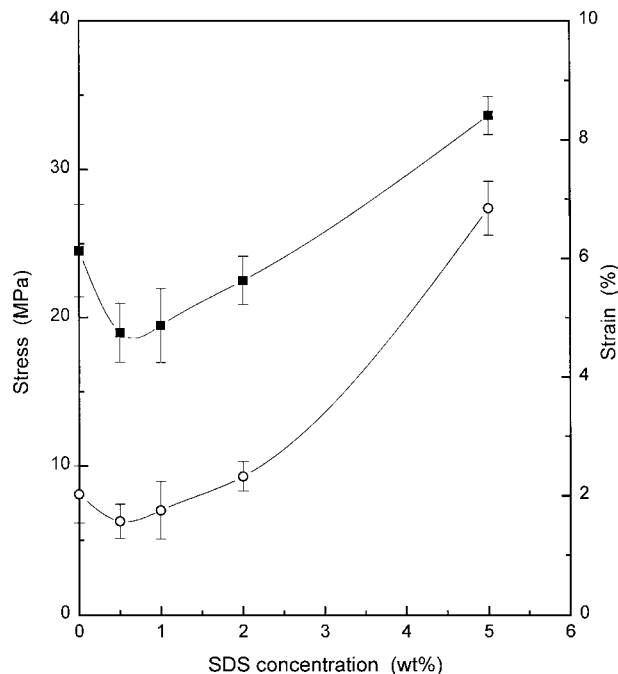


Figure 7 (■) Stress and (○) strain of 11S plastics as affected by SDS concentration.

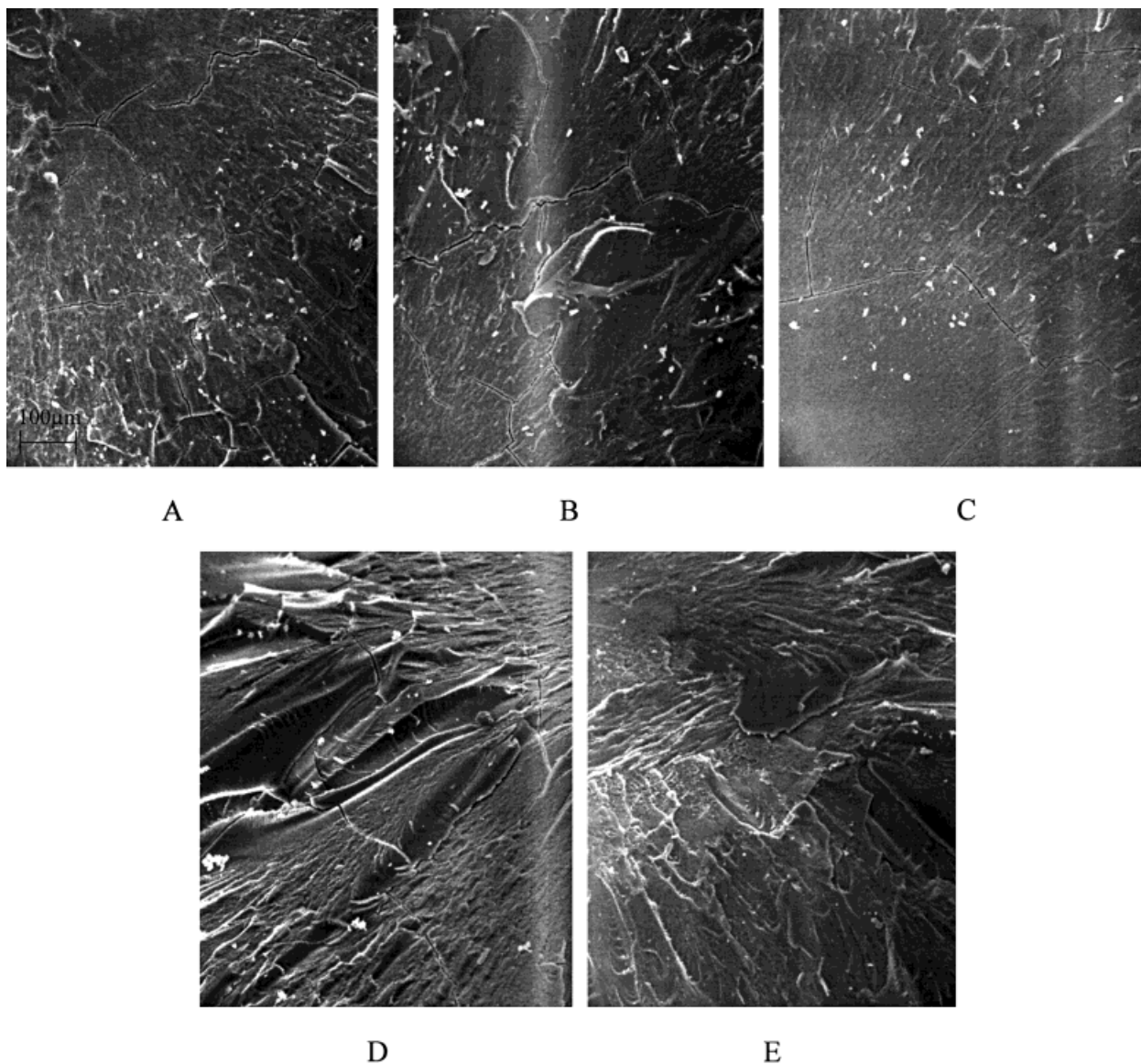


Figure 8 SEM photographs of (A) control, (B) 0.5% SDS-modified, (C) 1.0% SDS-modified, (D) 2.0% SDS-modified, and (E) 5.0% SDS-modified 11S plastics.

0.5% SDS-modified plastics were weaker than in the plastic with 5.0% SDS, and, hence, the plastic with 0.5% SDS had a lower σ_B and ϵ_B .

The fracture surfaces of the control and low-concentration SDS-modified 11S plastics were smooth and had some cracks [Fig. 8(A–C)], which are typical characteristics of brittle fracture. For the 2.0 and 5.0% SDS-modified 11S plastics [Fig. 8(D,E)], the fracture surfaces were rather coarse and fluctuant, displaying some characteristics of tough fracture. Furthermore, no cracks were observed in the fracture surface of 5.0% SDS-modified plastics [Fig. 8(E)]. These findings confirmed

that high-concentration SDS-modified 11S plastics had much better mechanical properties than those of the control plastics.

Water Absorption of Molded 11S Plastics

Modification by SDS had marked effects on the water absorption of 11S plastics. The water absorption of both control and modified plastics first increased sharply and then leveled off with a long soaking time (Fig. 9), indicating that the water absorption became saturated. With increasing SDS concentration, modified plastics absorbed

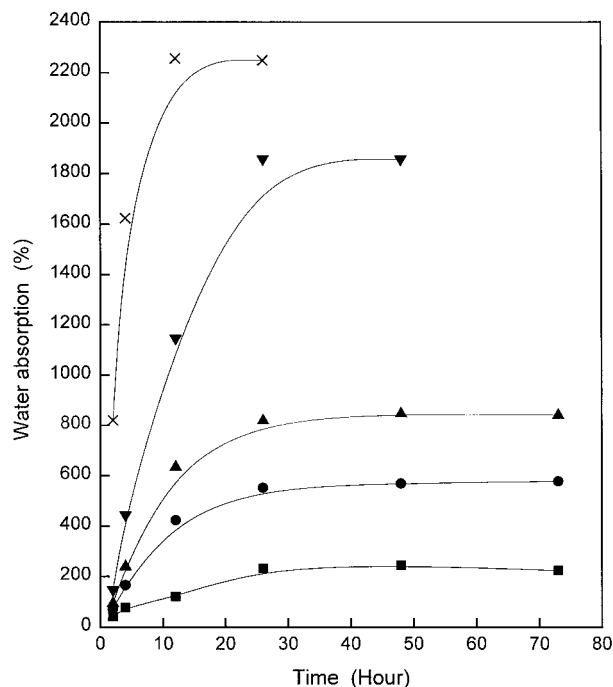


Figure 9 Water absorption of 11S plastics as affected by soaking time: (■) control, (●) 0.5% SDS-modified, (▲) 1.0% SDS-modified, (▼) 2.0% SDS-modified, and (x) 5.0% SDS-modified 11S plastics.

water more quickly and the 5.0% SDS-modified 11S plastics took only 12 h to reach saturation. The water absorption at any given time increased with increasing SDS concentration, indicating that SDS modification reduced the water resistance of 11S plastics. The high water absorption of SDS-modified plastics was believed to be due to an interaction between the hydrophobic moieties of SDS and the hydrophobic side chains of 11S, which reduced the hydrophobicity of 11S and increased the net charge of 11S plastics.

CONCLUSIONS

The SDS in 11S protein plastics acted not only as a denaturant but also as a plasticizer, resulting in a decrease in T_g as its concentration increased. The hydrophobic interaction between SDS molecules and 11S protein played an important role in determining the structure and properties of the 11S plastics. This interaction also resulted in recovery and/or reformation of the ordered structure of 11S during the freeze-drying process.

Properties of plastics made from SDS-modified 11S protein were dependent on the SDS concen-

tration. Modification of the 11S with a high concentration resulted in plastics with a coarse and tough fracture surface, high tensile strength and elongation, but greater water absorption.

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