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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Wang, S. , Sue, H. -J. and Jane, J.(1996) 'Effects of Polyhydric Alcohols on the Mechanical Properties of Soy Protein Plastics', Journal of Macromolecular Science, Part A, 33: 5, 557 — 569

To link to this Article: DOI: 10.1080/10601329608010878

URL: <http://dx.doi.org/10.1080/10601329608010878>

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EFFECTS OF POLYHYDRIC ALCOHOLS ON THE MECHANICAL PROPERTIES OF SOY PROTEIN PLASTICS†

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ABSTRACT

Polyhydric alcohols, i.e., ethylene glycol, glycerol, propylene glycol, 1,3-propanediol (trimethylene glycol), and polyethylene glycol (200 and 400), were investigated for their plasticizing effects on soy protein plastics. Tensile strength and percentage elongation at break of compres-

†Journal Paper J-16547 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, Project 3258.

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sion-molded soy protein specimens containing each of the polyhydric alcohols were measured, and Young's modulus was calculated. Ethylene glycol and glycerol demonstrated the greatest effects on the tensile properties. Differential scanning calorimetric (DSC) thermograms of soy protein with glycerol showed a major exothermic transition. Dynamic mechanical spectra showed that dry plastic specimens had a shear-storage modulus ($G' = 1.76$ GPa) about 50% larger than those of the high performance synthetic polymers tested. The shear-storage modulus was little dependent on temperature change up to ca. 130°C. After the specimens were moisturized at 50% relative humidity, the G' was reduced to 0.22 GPa. The shear-storage modulus of specimens containing 30% glycerol decreased when the temperature increased above -60°C. Rheological properties of soy protein with and without glycerol were evaluated by using a torque rheometer.

INTRODUCTION

Soy protein, the major component of the soybean (30–45%) [1], is a readily available biopolymer and a potential renewable source for biodegradable plastics. Soy protein, as a raw material, is competitive in price with conventional petroleum-based plastics and is desirable for making environmentally friendly, biodegradable disposable products, such as food containers, cutlery, outdoor sporting goods, and agricultural mulch films. Additionally, these biodegradable products, once they become waste, can be collected, ground, and reused as animal feed, soil conditioners, etc.

Soy protein mainly consists of the acidic amino acids of aspartic acid (asparagine) and glutamic acid (glutamine), nonpolar amino acids (glycine, alanine, valine, and leucine), basic amino acids (lysine and arginine), and less than 1% of cysteine [1]. About 90% of the soy protein are storage proteins, consisting of 35% conglycinin (7S) and 52% glycinin (11S) [2]. Molecular weights of the protein subunit are ca. 20,000 and 35,000 daltons [2]. Soy protein has an isoelectric point at ca. pH 4.5. At pH 4.5, the soy protein has the least net charge and, thus, is the most water-resistant. It has been demonstrated that when pH drops from 6 to 4.5, water absorption of the plastics decreases from ca. 80% to ca. 30% after 26 hours submersion in water at 25°C [3].

Great effort has been devoted to enhance the biodegradability of plastics. Starch and other biodegradable materials have been used as fillers in petroleum-based plastics [4–9], but results show that after the fillers were degraded, the petroleum-based polymers resist or are slow to biodegrade. Microbial-based polymers, such as poly(lactic acid) and poly(hydroxybutyrate), have good physical and mechanical properties for plastic products [10, 11]; however, the production costs are too high for many uses. Plastics made from starch alone are water-sensitive, disintegrate in water, and lack storage stability [12]. Starch acetate [13] and starch aldehyde [14] produce good plastics, but production costs are high. Among the different types of biodegradable polymers, soy protein has the advantages of being economically competitive and has good water resistance and storage stability.

Biodegradation of molded soy protein plastics in both a soil environment and in a simulated marine environment show a rapid conversion of the plastics into CO₂ and water [15]. The molded soy protein plastic degrades more quickly than the raw material, and soy protein/starch blended plastics are the most promptly degraded [15]. The differences in the degradation rates are attributed to the heat denaturation of protein and the balanced carbon and nitrogen sources in soy protein and starch blends [15].

Plastics made from soy protein alone are rigid and brittle. Proper plasticizers are needed to improve the properties of soy protein plastics. Polyhydric alcohols were selected for the study because of their similar polarities to soy protein. In this study we investigated various polyhydric alcohols [i.e., ethylene glycol, glycerol, propylene glycol, 1,3-propanediol (trimethylene glycol), and polyethylene glycol (200 and 400)] for their effects as plasticizers for soy protein plastics. The tensile properties, thermal properties, and the dynamic mechanical properties of soy protein plastics with and without polyhydric alcohol plasticizers were studied.

EXPERIMENTAL

Soy protein isolate (PRO-Fam 646, Archer Daniels Midland, Decatur, IL), containing more than 90% protein (dry basis), was used without further treatment. Ethylene glycol (reagent grade) and polyethylene glycol (MW 200 and 400, reagent grade) were products of Sigma Chemical Co. (St. Louis, MO). Propylene glycol, 1,3-propanediol, and glycerol (reagent grade) were products of Fisher Scientific (Pittsburgh, PA). All other chemicals were reagent grade and were used without further purification.

Type 1 test specimens (dumbbell shape, overall length 165 mm, ASTM Standards D-638-86) [16] were made from 15.0 g soy protein isolate by compression molding (Wabash compression-molding machine, Wabash Metal Products, Inc., Wabash, IN). Each of the polyhydric alcohols was added by drops to the soy protein powder in a Kitchen Aid Mixer (Model 4, Hobart MFG Co. Troy, OH) under stirring (200 rpm). The mixture was stirred at 200 rpm for 30 minutes to achieve homogeneity. Soy protein isolate containing ca. 8% water and various polyhydric alcohols ranging from 0 to 30% were molded at 140°C and 19.6 MPa for 6 minutes. After compression, the mold and specimen were allowed to cool to below 50°C before removing the specimens.

The tensile strength and percentage elongation at break of each specimen were measured by using an Instron Universal Testing System (Model 4502, Canton, MA), and the Young's modulus was calculated. The tests were performed according to the standard test methods for tensile properties of plastics (ASTM D-638-86). Specimens were preconditioned at 50% relative humidity for 40 ± 2 hours. Five or more specimens for each treatment were tested at 50 mm/min crosshead speed.

The thermal properties of soy protein with and without polyhydric alcohols were examined by using a differential scanning calorimeter equipped with an Intra-cooling II System and a Thermal Analysis Data Station (DSC-7, Perkin-Elmer, Norwalk, CT). Aluminum pans were used for the analysis, and 25 mg samples were used for the analysis. The heating rate was 10°C/min. Enthalpy changes were

computed automatically by the data station, based on the melting of an indium standard.

The dynamic mechanical properties of the soy protein plastics were analyzed by using a Rheometrics RMS-805 rheometer (Rheometrics, Piscataway, NJ). Samples used for the test had a size of $6.25 \times 1.25 \times 0.31$ cm. A strain amplitude of 0.05% under torsional mode, and a frequency of 1 Hz were used for the test. Soy protein plastic samples used for the test were compression-molded with a molding mixture of 7% moisture content. Dry soy protein plastic samples were prepared by drying the samples in a vacuum oven at 60°C, 30 mmHg, for 14 hours. Moisturized samples were prepared by equilibrating the samples at 50% relative humidity for 3 weeks.

The torque rheological properties of soy protein with water and with water and glycerol were studied by using a torque rheometer with a mixer measuring head and a fixed blade roller with electric heating (Brabender Plastic-corder, PL 2000, C. W. Brabender Instruments, Hackensack, NJ). Soy protein (80.00 g) and plasticizers were added to the mixer manually; a 5-kg load was used for the test, and the mixing speed was set at 16 rpm for 55.0 minutes. The tests were conducted following the Standard Testing Method of ASTM D-3795-79 [17].

RESULTS AND DISCUSSION

Without a plasticizer, soy protein plastics are rigid and brittle [3]. A stress-strain plot of a molded soy protein plastic specimen is shown in Fig. 1(A). To increase flexibility and elasticity of soy protein plastics, various chemicals were tested as plasticizers. Polyhydric alcohols, e.g., ethylene glycol, glycerol, propylene glycol, 1,3-propanediol (trimethylene glycol), and small-molecular-weight polyethylene glycols, displayed good compatibility with soy protein and were considered as potential plasticizers. Among the plasticizers tested, ethylene glycol (Fig. 2), glycerol (Fig. 3), and propylene glycol (Fig. 4) displayed the greatest effects on the tensile strength and the percentage elongation at break of the plastic specimens. A stress-strain plot of a soy protein plastic specimen containing 25% (w/w) glycerol is shown in Fig. 1(B). At the 30% (w/w) concentration level, the plastic specimens containing ethylene glycol displayed ~400% elongation at break, compared with those containing glycerol (330%) and propylene glycol (120%). This may be attributed to the small molecular weight and greater polarity of the compounds. 1,3-Propanediol was less polar and less effective than those three in changing the tensile properties of soy protein plastics. At a 30% concentration, the plastic specimens containing 1,3-propanediol displayed ca. 16% elongation (Fig. 5). Polyethylene glycol 200 and 400, having ca. 4 and 8 average repeating units, respectively, showed no significant effects on percentage elongation at break of the plastic specimens (Figs. 6 and 7).

In addition to the effects of the polyhydric alcohols on the mechanical properties of the plastics, toxicity of the chemicals is another major concern for their application. Glycerol is nontoxic. Propylene glycol has a very low order of toxicity but is more volatile [18]. Ethylene glycol, however, is classified as hazardous for food-related uses. On the basis of these considerations, glycerol seems to be the most suitable plasticizer for soy protein plastics.

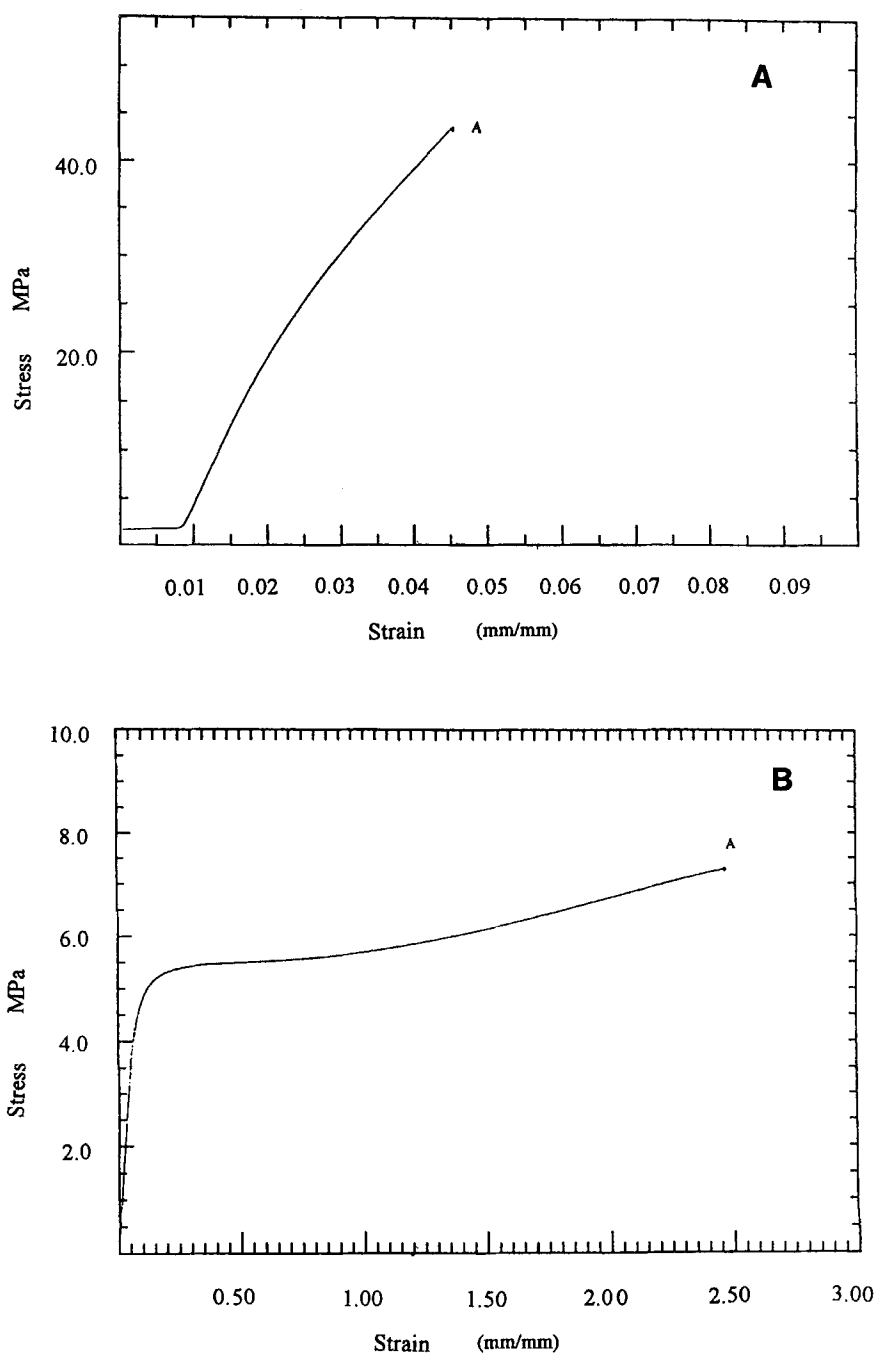


FIG. 1. Stress-strain plots of compression-molded soy protein plastics. (A) Soy protein containing 7.1% moisture. (B) Soy protein containing 7.1% moisture and 25% (w/w) glycerol. Processing conditions: temperature 140°C, pressure 19.6 MPa, and 6 minutes.

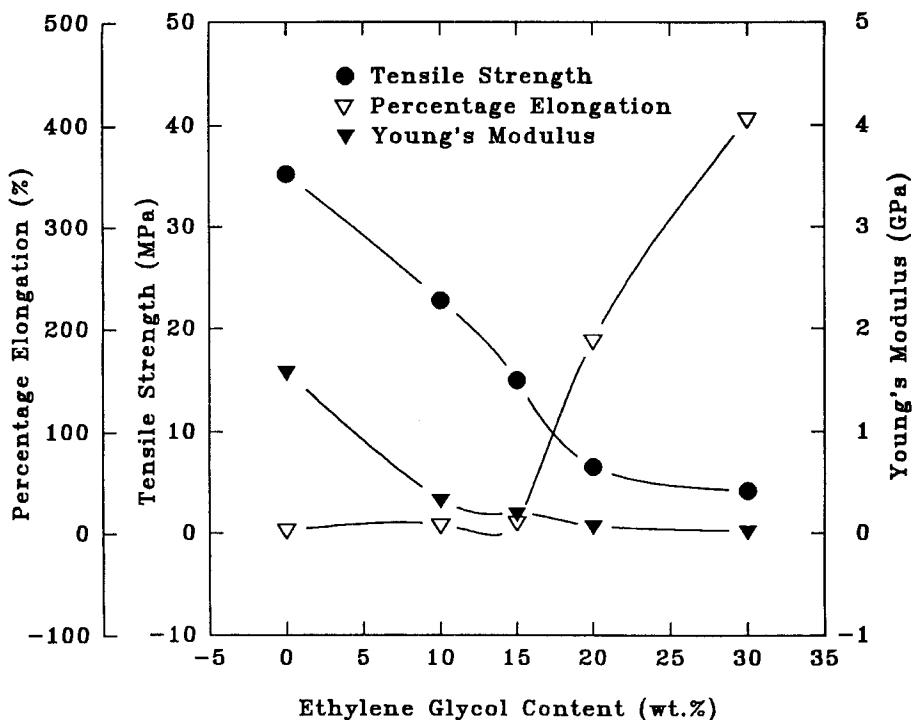


FIG. 2. Effect of ethylene glycol content on the mechanical properties of compression-molded soy protein plastics. The moisture content of the soy protein isolate was 8.2%.

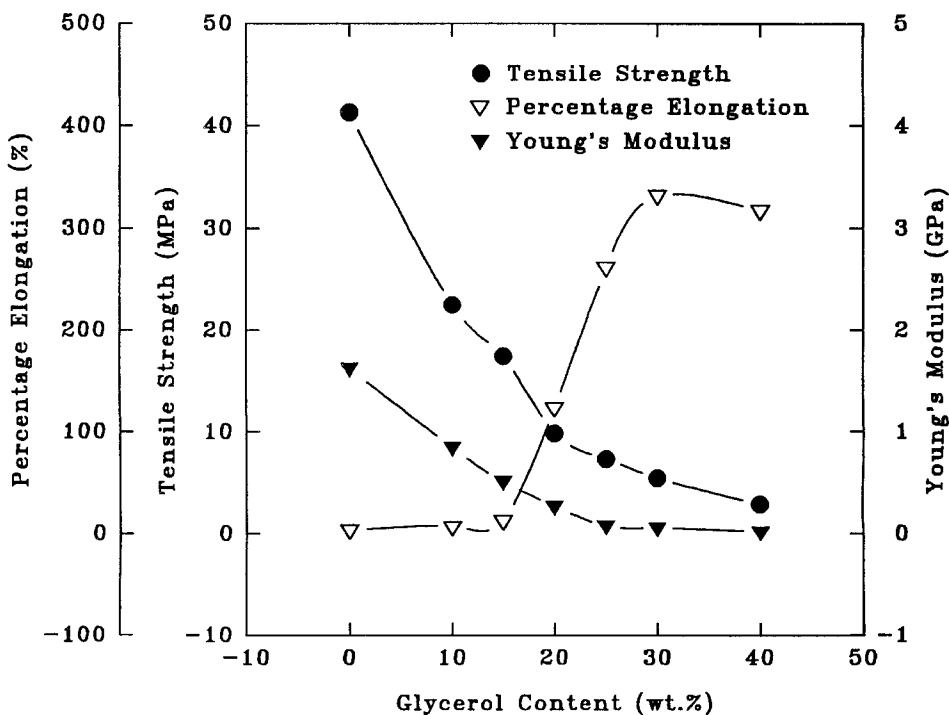


FIG. 3. Effect of glycerol content on the mechanical properties of compression-molded soy protein plastics. The moisture content of the soy protein isolate was 7.1%.

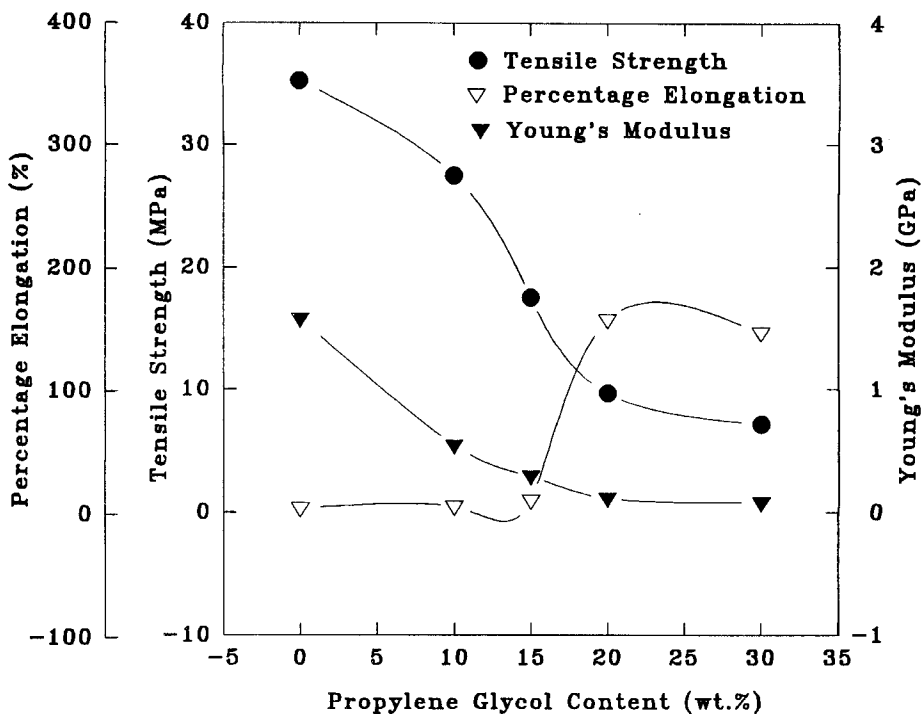


FIG. 4. Effect of propylene glycol content on the mechanical properties of compression-molded soy protein plastics. The moisture content of the soy protein isolate was 8.2%.

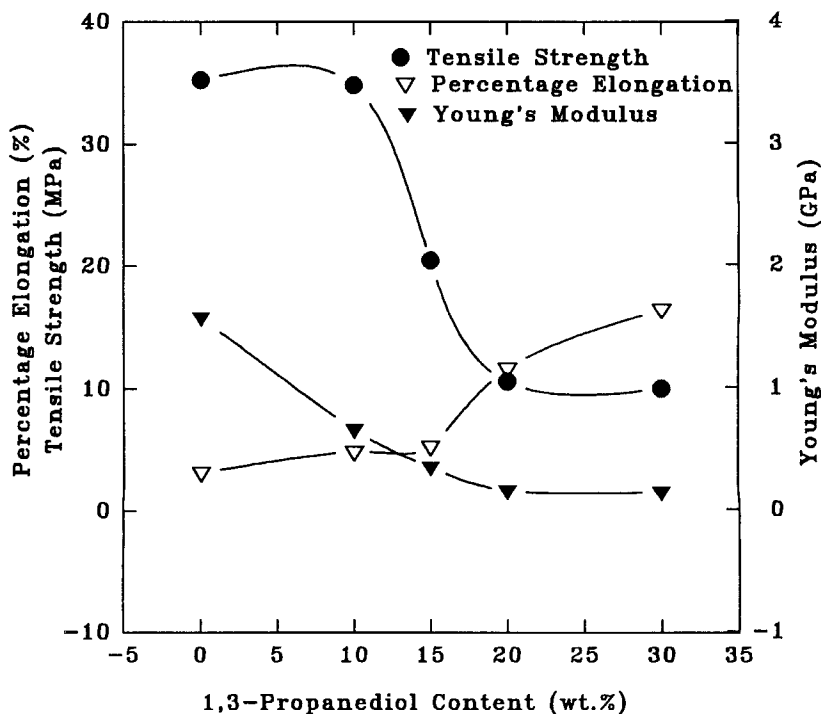


FIG. 5. Effect of 1,3-propanediol content on the mechanical properties of compression-molded soy protein plastics. The moisture content of soy protein isolate was 8.2%.

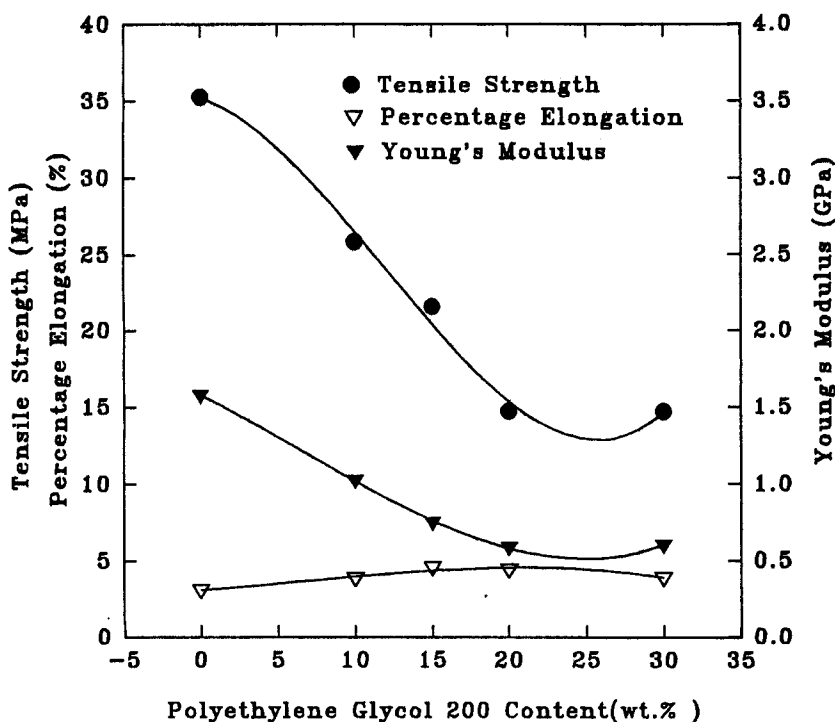


FIG. 6. Effect of polyethylene glycol 200 content on the mechanical properties of compression-molded soy protein plastics. The moisture content of soy protein isolate was 8.2%.

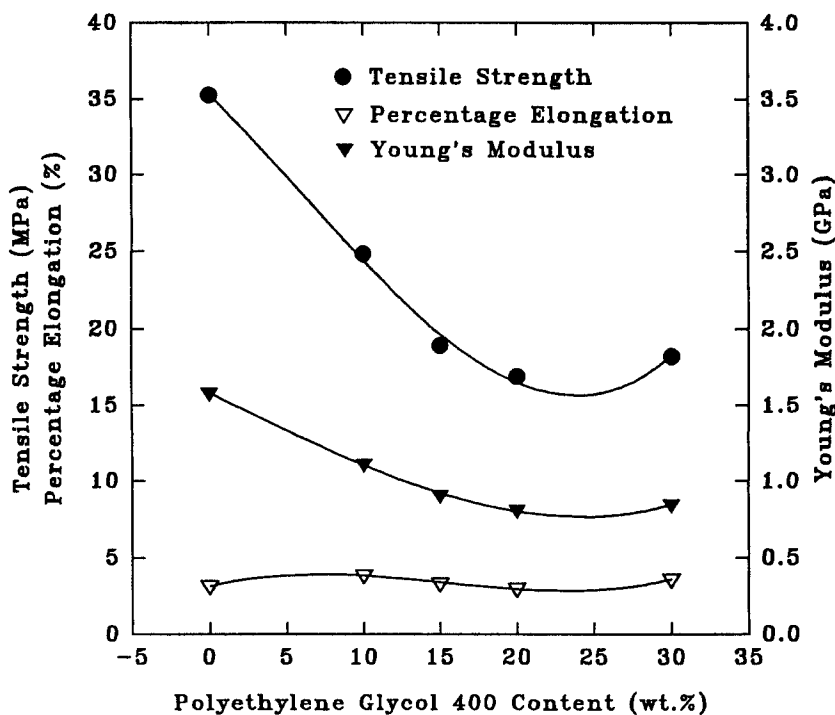


FIG. 7. Effect of polyethylene glycol 400 content on the mechanical properties of compression-molded soy protein plastics. The moisture content of soy protein isolate was 8.2%.

Differential scanning calorimetric (DSC) thermograms showed endothermic transitions followed by an exothermic transition when soy protein was heated in an aqueous system (Fig. 8). The thermograms of the commercial soy protein isolate did not exhibit the typical melting of 7S and 11S protein (at ca. 120°C and 150°C with 10% water content), indicating that the commercial protein product was denatured. The thermograms showed a minor peak at ca. 50°C and a major exothermic peak at ca. 160°C. Additional studies are needed to identify the nature of the peak at 50°C.

Because protein aggregation is an exothermic reaction [19], the exothermic peak at 160°C may be attributed to aggregation of the protein. The DSC thermogram of soy protein with glycerol, however, showed an exothermic transition at ca. 70°C (Fig. 9). The peak temperature and the enthalpy change of the exothermic transition increased with an increase of glycerol concentration. The exothermic peak may be attributed to an unfolding of the native soy protein structure that resulted from a favorable interaction of glycerol with the hydrophobic amino acids which are folded inside the native protein [20].

Without polyhydric alcohols as plasticizers, and when the material remained dry, the soy protein plastic had a large shear-storage modulus ($G' = 1.76$ GPa). The shear-storage modulus remained large and was temperature insensitive up to ca. 130°C as shown by dynamic mechanical spectroscopy (Fig. 10). This shear-storage modulus curve was about 50% greater than those of the high performance synthetic polymers tested (Table 1) [21]. The extremely large shear-storage modulus may be

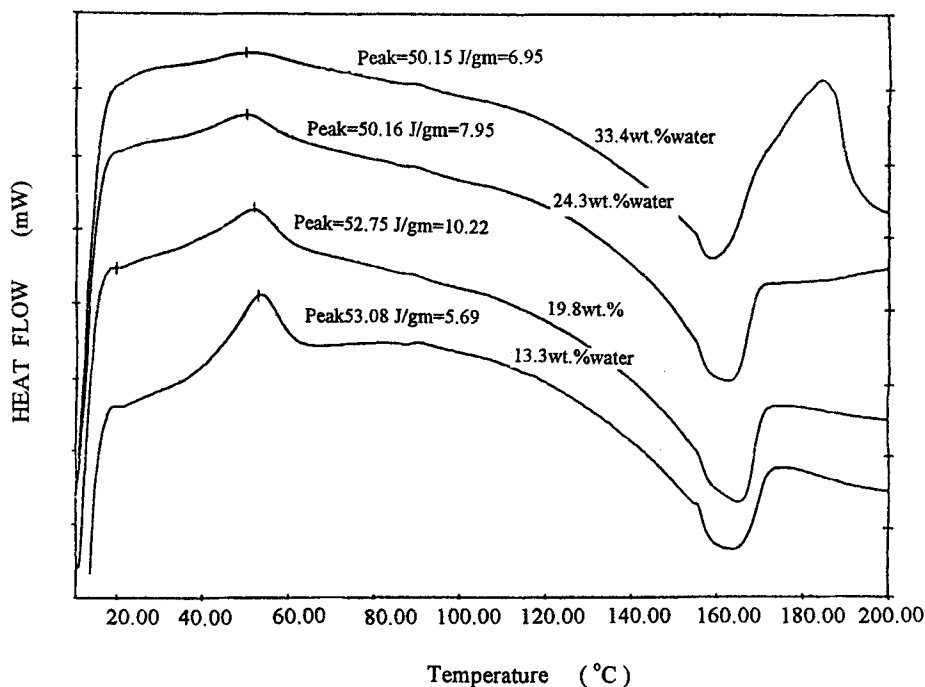


FIG. 8. DSC thermograms of soy protein isolate with water only. Scanning rate: 10.0°C/min.

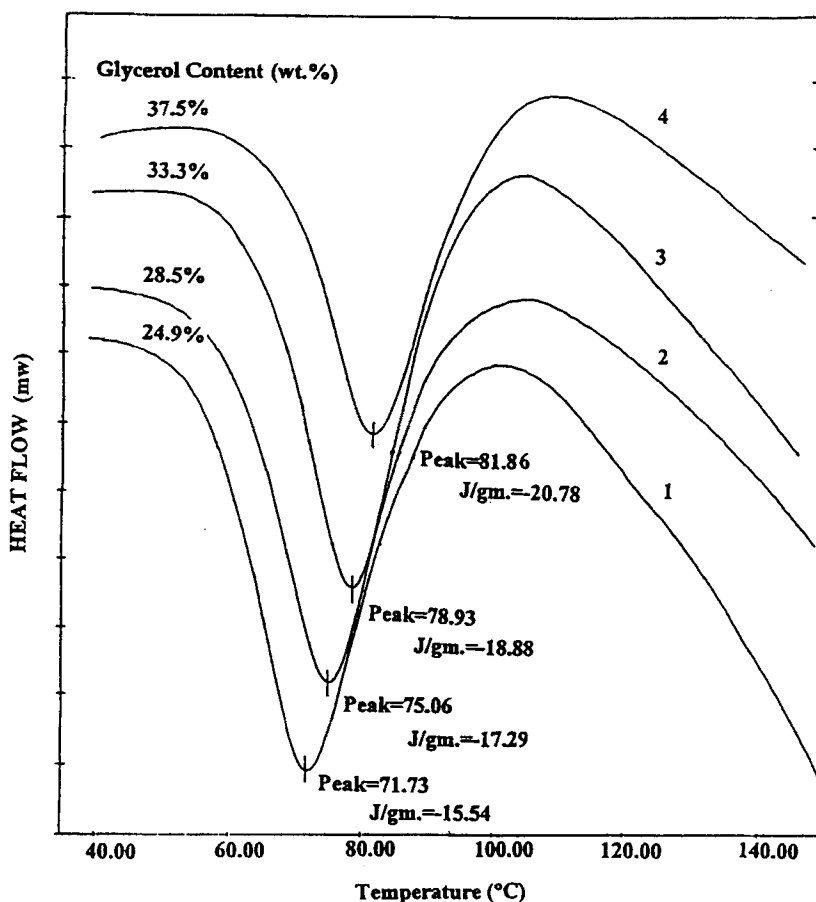


FIG. 9. DSC thermograms of soy protein isolate with glycerol. Moisture content: 6.5%. Scanning rate: 10.0°C/min.

attributed to 1) charge-charge and dipole-dipole interactions between amino acid side chains result in crosslinking effects and 2) the soy protein matrix contains approximately 7-10% by volume of spherical protein particles having diameters of 5-40 nm. These soy protein particle inclusions may have served as rigid fillers to stiffen the soy protein matrix and as tougheners to contribute to the fracture property the system exhibits.

After the soy protein plastics were moisturized at 50% relative humidity for 3 weeks, the G' was reduced by an order of magnitude ($G' = 0.22$ GPa) compared with that of the plastics at the dry state. The G' of the moisturized sample was significantly affected by temperature variation at 50°C and above. With 30% glycerol in the sample, the soy protein plastic displayed an even larger G' than that of the dry sample when the temperature was kept below -60°C. At temperatures above -60°C, the G' significantly decreased as temperature increased.

This observation indicates that soy protein has the potential to compete with engineering polymers if the soy protein plastic can be kept dry. The presence of

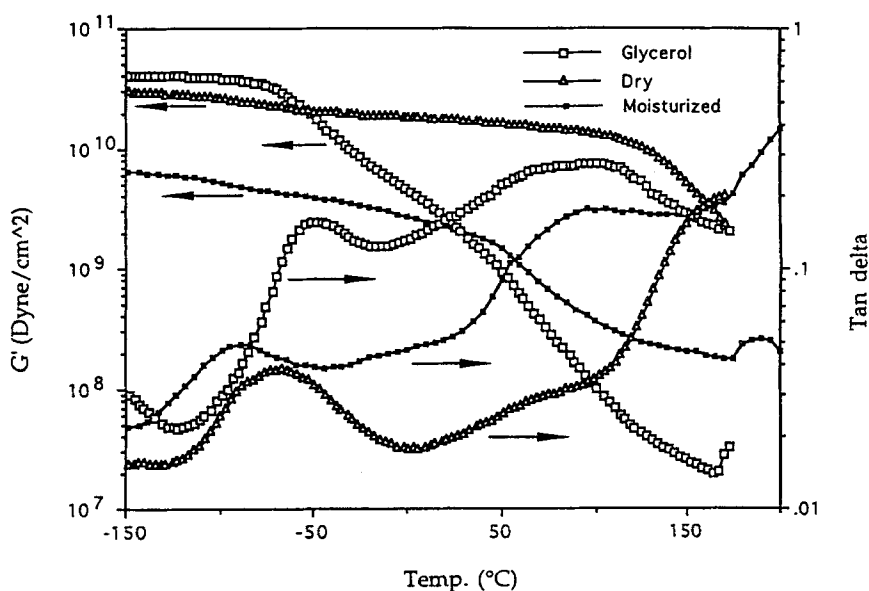


FIG. 10. Dynamic mechanical spectra (frequency = 1 Hz) of soy protein isolate with and without moisture and glycerol.

moisture in soy protein gives rise to an overall increase of the $\tan \delta$ curve. This suggests that moisture may act to assist and promote energy dissipating molecular motions, especially at temperatures above 50°C . The addition of glycerol to soy protein resulted in an interesting, also intriguing, phenomenon. The cause for the greater G' than that of the dry soy protein at -60°C and below may be attributed to the solidified glycerol. The immobile glycerol molecules fill the space between the soy protein molecules and hinder the motion of protein molecules. This stiffens the soy protein matrix. Once the temperature is above the freezing temperature of glycerol (-60°C), the molecular interaction between the soy protein and the glycerol allows the soy protein molecules to easily slip by one another. This may be responsible for the tremendous drop in G' with respect to temperature. Phase

TABLE 1. Shear-Storage Modulus and Glass Transition Temperature of Selected Plastics

	G' at 25°C , GPa	T_g , $^{\circ}\text{C}$
Soy protein (dry)	1.76	≈ 150
Soy protein (moisturized)	0.22	≈ 150
Soy protein (glycerol)	0.21	≈ -50
Epoxy	1.20	145
Polycarbonate	0.93	155

TABLE 2. Torque Rheological Properties of Soy Protein Isolate^a

Ingredients						
Soy protein isolate	Glycerol, wt%	H ₂ O	Material temperature, °C	Mixer temperature, °C	Roller speed, rpm	Torque, Mg
70		30	75	98	16	3,500
70.2	25	4.8	91	130	16	> 11,200
60.8	35	4.2	73	136	16	3,200
59.8	25	15.2	74	120	16	2,200

^aTest conditions. Mixer type: Roller electrically heated. Test time: 55.0 minutes. Load, chute: Manual + 5 kg. Sample weight: 80.00 g.

morphology analysis and fracture phenomenon studies of the plastic samples have been examined by using transmission electron microscopy with dry protein plastic samples; the results will be reported separately.

The rheological properties of soy protein with and without glycerol were evaluated by using a torque rheometer (Table 2). Without adequate plasticizers (water and glycerol), the torque test was difficult to perform because the torque of the protein was too high (over 10,000 Mg) for operation of the machine. When the concentration of glycerol increased from 25 to 35%, the torque of the material decreased from > 11,200 to 3200 Mg.

The results obtained from this study indicated that polyhydric alcohols have better interactions with the hydrophobic portion of the protein, whereas water reduces the force of charge and dipole-dipole interactions of the protein. A combination of water and polyhydric alcohols presents the best plasticizing effect.

CONCLUSION

Glycerol, ethylene glycol, and propylene glycol were better plasticizers than 1,3-propanediol. Polyethylene glycol 200 and 400 had little effect on the percentage elongation at break of the plastics. Glycerol induced a major exothermic transition to DSC thermograms of soy protein, which was attributed to the interaction between glycerol and the hydrophobic amino acids of the protein. Dry soy protein plastic displayed an extremely large shear-storage modulus, 50% larger than the high-performance engineering plastics of epoxy and polycarbonate tested in the study.

ACKNOWLEDGMENTS

The authors thank the United Soybean Board and the Iowa State University Center for Advanced Technology Development for financial support of this research.

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