Effects of Molding Temperature and Pressure on Properties of Soy Protein Polymers

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ABSTRACT: Because of the worldwide environmental pollution problem with petroleum polymers, soy protein polymers have been considered as alternatives for biodegradable plastics. The objective of this research was to study the curing behavior of soy protein isolates (SPIs) for that application. The molding variables of temperature, pressure, and time and curing quality factors of tensile strength, strain, and water resistance were evaluated. The maximum stress of 42.9 MPa and maximum strain of 4.61% of the specimen were obtained when SPI was molded at 150°C and 20 MPa for 5 min. The water absorption of the specimen decreased as molding temperature and time increased. Glycerol greatly improved the flexibility of the specimen but decreased its strength. For SPI with 25% glycerol added, the maximum stress and strain of about 12 MPa and 140%, respectively, were achieved when the specimen was molded at 140°C for 5 min. Molding temperature, pressure, and time are major parameters influencing the curing quality of soy protein polymers. At fixed pressure, the molding temperature and time had significant interactive effects on curing quality. At high temperature (e.g., at 150°C) it took about 3 min to reach optimum curing quality; however, at low temperature (120°C) it took about 10 min to reach optimum curing quality. The maximum strength and strain of the cured protein polymer occurred at the molding temperature close to its phase transition temperature or about 40°C below its exothermic temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2595-2602, 1999

Key words: curing effect; mechanical property; soy protein polymer; plastics; glycerol

INTRODUCTION

About 21.9 billion lbs of plastic waste were discarded in 1992, and this figure is expected to reach 34.2 billion by 2002.¹ Although petroleum-based plastics are cheap and have very diverse applications, their market has been threatened by the inevitable increase in price and worldwide environmental concern. Research and development of biodegradable plastics from renewable resources including protein,²⁻⁴ starch,⁵⁻⁸ and microbial fermentation products⁹⁻¹¹ have been conducted recently. Among these renewable polymers, soy protein is relatively low cost and abundant. The possible uses of soy proteins for adhesives,^{12,13} coating polymers,^{12,14} plastics,¹⁵⁻¹⁹ and edible packaging films²⁰⁻²² have been investigated recently.

Soy protein is classified as a globulin with mainly polar amino acids including acidic and basic amino acids and nonpolar amino acids. About 90% of the protein in soybeans is storage protein. The major components of soy protein are

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conglycinin (7S, about 35%) and glycinin (11S, about 52%). The 7S and 11S proteins both have quaternary structures with disulfide bonds binding the polypeptide subunits together.²³ Temperature and pressure are two main parameters in plastic processing. Proteins and their subunits will unfold, interact, and entangle with each other at elevated temperature and pressure. Therefore, the intermolecular strength is significantly influenced by the processing temperature and pressure and pressure employed.

Paetau et al. and Huang found that the tensile strength of soy protein plastics were significantly affected by molding temperatures and initial moisture content.^{15,16} Soy protein plastics prepared from soy protein powder with 11.7% moisture content had a tensile strength of 40 MPa at a 140°C molding temperature, whereas the tensile strength was 35 MPa at a 125°C molding temperature.¹⁵ Jane and Wang reported that the tensile strength of an injection-molded soy protein based specimen was 8.73 MPa at 135°C (zone 1) and 145°C (zone 2) molding temperatures, but it was 5.39 MPa at 135°C (zone 1) and 150°C (zone 2) molding temperatures.¹⁷

Soy proteins are complex macromolecules consisting of various amino acids. Along the main chain there are various side chains attached to the amino acids. Any chemical, physical, or enzymatic treatment will cause changes in the molecular structure, resulting in different physical properties. Various chemical treatments and plasticizers have been investigated to improve the brittleness and water resistance of sov protein polymers. Paetau et al. prepared testing tensile bars from soy protein polymers with various chemical treatments at a 160°C molding temperature and found that soy proteins that had been subjected to acid and glyoxal treatment and adipic/acetic anhydride crosslink treatment had lower tensile strength but higher water resistance than nontreated soy proteins.¹⁸ Wang et al. prepared testing tensile bars from soy proteins in the presence of various plasticizers at a 140°C molding temperature.¹⁹ They found that glycerol, ethylene glycol, and propylene glycol were better plasticizers for soy proteins than 1,3-propanediol and that polyethylene glycol 200 and 400 gave little improvement in the extensibility of the plastics.¹⁹ Jane and Wang also prepared testing tensile bars from soy proteins in the presence of various levels of glycerol and water at fixed a molding temperature.¹⁷ They found that glycerol and water both significantly increased the flexibility but greatly decreased the tensile strength of the soy protein plastics.

Like many polymers, soy proteins may change their phases when they are exposed to great temperature changes. Phase transition temperatures are defined as the temperature ranges at which the polymers change their phases. The phase transition temperature is often affected by many factors including molecular structure, composition, and chemical or enzymatic treatment. Therefore, phase transition is a temperature-, time-, and composition-dependent, materials-specific change in physical state. Many properties of the polymer, especially mechanical and rheological properties, are strongly related to its phase transition temperature and processing conditions, especially temperature. Soy proteins with different chemical treatments or different levels of plasticizers may have different phase transition behavior and, consequently, different optimum processing conditions, which must be used to produce better quality plastics. The objective of this article was to study the plastic curing behaviors of soy proteins alone and in the presence of glycerol at various molding temperatures, pressures, and times associated with phase transition.

EXPERIMENTAL

Materials and Specimen Preparation

Soy protein isolate (SPI, PRO-Fam 970, Archer Daniels Midland, Decatur, IL) was prepared by acid precipitation and contained more than 90% protein (dry basis).^{24,25} The glycerol was the product of Fisher Scientific (Pittsburgh, PA).

To prepare the SPI specimen, 5.0 g of soy protein powder with 6.5% moisture content was placed in a dogbone-shaped tensile bar mold (type IV) and compression molded using the Carver Hot Press (model, 3890 Auto M, Carver Inc., Wabash, IN) according to ASTM standard D686-92.²⁶ Then the specimen was cooled to room temperature before removal from the mold. Flash was removed carefully by sanding the edges of the specimen with grade 180 abrasive sandpaper. To prepare the SPI with the plasticizer specimen, glycerol was added to the protein powder in drops and mixed in a mixer (International MFG, Co., NB) for 45 min at room temperature. The mixture was equilibrated for 12 h. Then the same molding procedure was used as for the SPI alone.

Experimental Design

Molding variables included temperature, pressure, and time. To observe the effects of molding pressure on soy protein plastic performance, SPI specimens were molded at molding pressures of 5, 10, 20, 40, and 60 MPa at 150°C for 3 min. To study the effects of molding temperature and time on the curing behavior of the protein polymer, SPI specimens were molded at various temperatures and times at a 20-MPa molding pressure. A 5×4 \times 1 full factorial experimental design was used with molding temperatures of 100, 120, 140, 150, and 160°C and molding times of 3, 5, 10, and 15 min. To observe the curing behavior of SPI in the presence of glycerol, another $5 \times 4 \times 1$ full factorial experiment was conducted using the same range of temperatures, times, and pressures.

Thermal Analysis

Thermal phase transition behaviors of SPI powders with and without glycerol were measured using the differential scanning calorimeter (DSC, Perkin–Elmer, Norwalk, CT), which was calibrated with indium and zinc before official measurements. The temperature scan range was from 20 to 200°C at a heating rate of 10°C/min.

Mechanical Property Tests

Mechanical properties were measured using an Instron testing system (model 4466, Canton, MA) according to the Standard Test Method for Tensile Properties of Plastics (ASTM D638-92).²⁶ Each specimen was preconditioned at 50% relative humility for 48 h and tested at 5 and 50 mm/min crosshead speeds for the SPI specimen and SPI with glycerol specimen, respectively. The stress, strain (%) at maximum stress, and Young's modulus were calculated.

Water Absorption and Microstructure

Water absorption was measured using the modified ASTM standard method (D570-81).²⁷ The specimens were preconditioned by drying them in an oven at 50°C for 14 h, then they were cooled in a desiccator for a few minutes and weighed. The preconditioned specimens were submerged in distilled water at 25°C for 2 and 26 h. The specimens were removed from the water and dried with a paper towel before weighing. Dry matter from the plastics left in the water during soaking was also included in the water absorption calculation. The

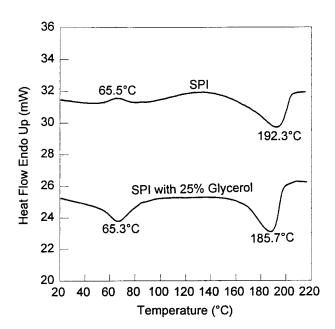


Figure 1 Differential scanning calorimetric thermograms of soy protein isolate (SPI) powder and SPI powder with 25% glycerol.

microstructure of the fractured surface of selected plastic specimens was observed using a scanning electron microscope (SEM, AutoScan, ETEC Corporation) at an accelerated voltage of 20 kV.

RESULTS AND DISCUSSION

DSC Thermal Transition Properties

The DSC thermograms of SPI and SPI with 25% glycerol are shown in Figure 1. For the SPI sample, an endothermic transition at 65.5°C followed by an exothermic transition at 192.3°C was observed. For the SPI with glycerol sample, two exothermic transitions were observed at 65.3 and 185.7°C. Similar DSC patterns were reported by Wang et al.¹⁹ in 1996. However, for 7S and 11S globulins segregated in our laboratory with about 8% moisture content, crystal melting phase transitions were observed at about 140 and 165°C (data not shown). The commercial soy proteins were denatured by various pretreatments and modifications, resulting in no crystal melting transitions but an exothermic transition, which may have been caused by protein aggregation.²⁸ Small molecules, such as water, in the protein system acted as plasticizers, which reduced protein exothermic temperature. For example, the exothermic temperatures were 160°C for SPI with

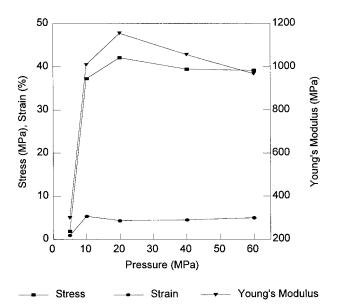


Figure 2 Effects of molding pressures on mechanical properties of soy protein isolate (SPI) plastics. The SPI plastic specimen was compression molded at 150°C for 3 min.

33.4% moisture content¹⁹ and 192°C for SPI with 6.5% moisture content. The exothermic peak temperature of SPI with 25% glycerol was 185°C, which was lower than that of SPI alone (192°C). As a plasticizer, glycerol improved the mobility of soy protein polypeptide chains, which then might interact easily with each other at an elevated temperature. Thus, soy protein in the presence of glycerol may aggregate at a lower temperature than soy protein alone.

The SPI had a small endothermic peak at around 65° C, which indicates that a special crystal structure might have formed during SPI pretreatment or modification. This peak area was reduced as glycerol content increased up to 20% and then changed into an exothermic peak as glycerol content increased to 25%. The exothermic peak of SPI with 25% glycerol at 65° C could have been caused by some unknown reaction or interactions between soy protein components and glycerol, which need to be studied further.

Effect of Curing Pressure

Stress increased sharply when pressure increased from 5 to 10 MPa, a maximum stress of 42.2 MPa was obtained at a pressure of 20 MPa, and then the stress decreased and maintained a value of about 39 MPa as pressure continued to increase. The Young's modulus showed a similar trend, reaching a maximum value (1156 MPa) at a pressure of 20 MPa. Strain at maximum stress increased sharply from 0.9 to 5.4% as pressure increased from 5 to 10 MPa, respectively, and remained relatively steady at around 4.5% as pressure continued to increase (Fig. 2).

Water absorption was reduced from 127 to 43.6% (2-h water soaking) for specimens prepared in the pressure range from 5 to 20 MPa and then increased slightly as pressure continued to increase (Fig. 3). In the low pressure range (5–20 MPa), as pressure increased the protein molecules were compacted tightly, resulting in a small void and, consequently, low water uptake. As pressure continued to increase, protein unfolding and interactions between proteins might have been inhibited, resulting in a slightly higher water uptake.

Effect of Curing Temperature and Time

Figures 4 and 5 show the interactive effects of molding temperature and time on the tensile strength and elongation of the soy protein plastics at 20 MPa molding pressure. The time required for soy protein to reach the maximum curing quality (maximum tensile strength and elongation and minimum water uptake) was longer at a lower temperature than at a higher temperature. For example, at a molding temperature of 120°C

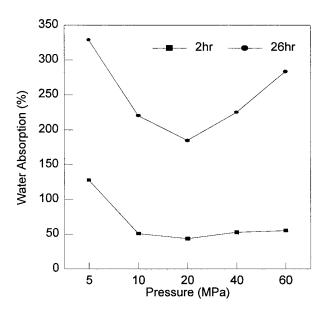


Figure 3 Effects of molding pressures on water absorption of soy protein isolate (SPI) plastics. The SPI plastic specimen was compression molded at 150°C for 3 min.

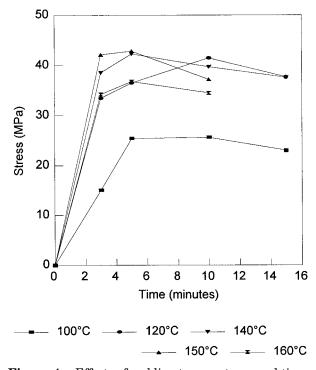


Figure 4 Effects of molding temperatures and times on stress properties of soy protein isolate (SPI) plastics. The SPI plastic specimen was compression molded at 20 MPa molding pressure.

the soy protein plastic took about 10 min to reach maximum curing quality, whereas at 150°C the curing process took about 3 min. The curing energy required could be expressed as a function of temperature and time,

$$E \propto f(T,t)$$

where T is the temperature in degrees Celsius, t is the time in hours, and E is the energy. The energy required for soy protein to reach maximum curing quality could be similar with a high temperature and short time or a low temperature and long time.

In the molding temperature range from 140 to 150°C, the maximum curing quality was similar at optimum curing conditions [Fig. 6(A-C)]. However, at molding temperatures of 100 and 160°C, the maximum curing quality was poor, for example, the tensile strengths were only 25 and 35 MPa, respectively. During the thermal curing process, the color of the soy protein specimen changed from powderlike white yellow (100°C) to transparent brown (150°C) and to dark brown

(160°C) as the molding temperature increased. Figure 7 shows the microstructure of the plastics prepared at different temperatures. The plastics prepared at 100°C [Fig. 7(A)] had a granular structure and more voids as compared to that prepared at 120°C [Fig. 7(B)]. As the temperature increased to 150°C, the protein melted completely, resulting in a continuously smooth structure [Fig. 7(C)]. At 160°C the protein became overheated and degraded, resulting in some small fragments and voids in the continuous protein phase [Fig. 7(D)]. At high temperatures the long peptide chains of the protein might be broken down, resulting in smaller peptide fragments. Deamination and decarboxylation might also happen, producing gas that might influence the interactions between protein molecules. Although the strength of the plastics prepared at 120 and 160°C was similar, the first was due to incomplete melting and the other was due to heat degradation. The plastics with smooth and continuous structures were significantly stronger in tensile strength and elongation compared to the plastics with the loose and void structures.

The interactive effects of molding temperature and time on tensile strength and elongation of soy

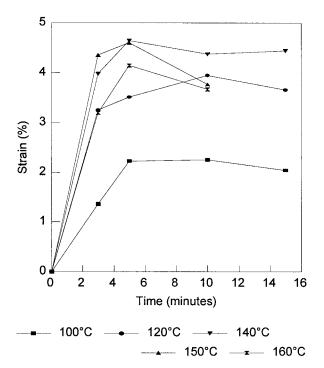


Figure 5 Effects of molding temperatures and molding times on strain properties of soy protein isolate (SPI) plastics. The SPI plastic specimen was compression molded at 20 MPa molding pressure.

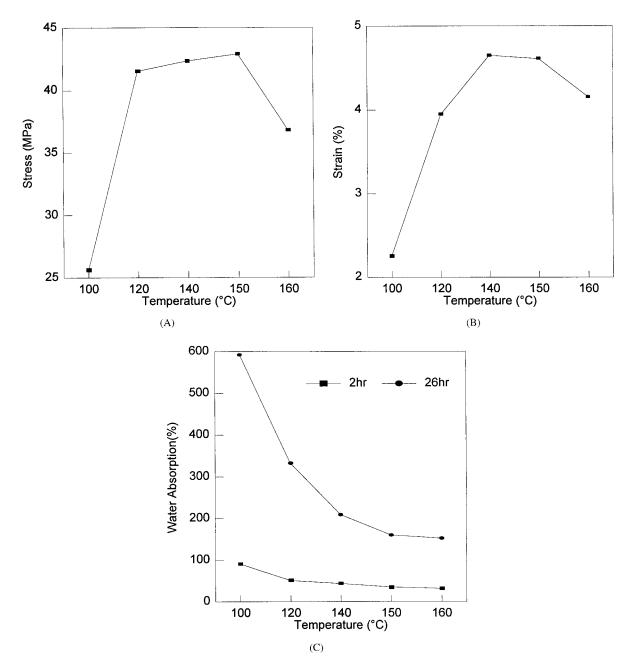


Figure 6 Maximum curing quality of soy protein isolate (SPI) plastics: effects of molding temperature on (A) maximum stress, (B) maximum strain, and (C) minimum water absorption of the SPI plastics molded at 20 MPa. Molding times were 10, 10, 5, 5, and 5 min for molding temperatures of 100, 120, 140, 150, and 160°C, respectively.

proteins in the presence of 25% glycerol were similar to the results for SPI alone. However, the highest tensile strength and elongation occurred at the 140°C molding temperature (Fig. 8). Optimum molding times were 10, 10, 5, 5, and 3 min with molding temperatures of 100, 120, 140, 150, and 160°C, respectively. Similar trends were also observed for strain. These results indicated that soy protein polymers may have a phase transition temperature at which the protein molecules start to unfold and interact to form a smoothed and entangled structure. This phase transition could not be seen from the DSC thermograms (Fig. 1) because of the predenaturation treatment. How-

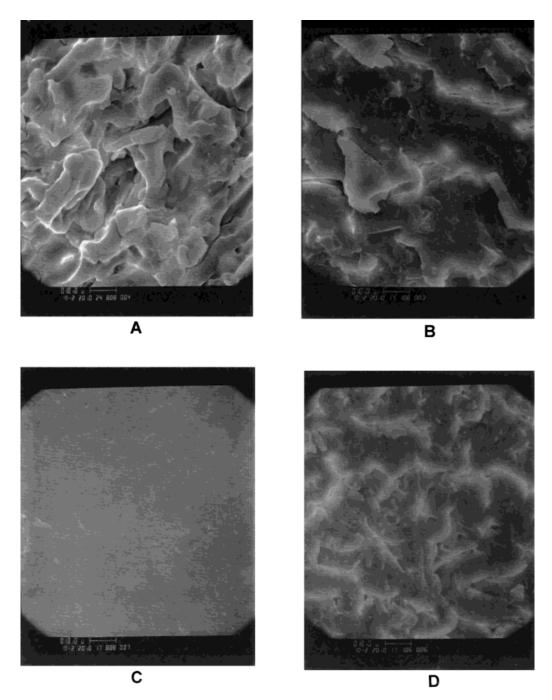


Figure 7 Microstructure of soy protein isolate (SPI) plastic specimens compression molded at 20 MPa for 5 min at (A) 100°C, (B) 120°C, (C) 150°C, and (D) 160°C.

ever, the "optimum" molding temperatures (150 and 140°C) for SPI and SPI with glycerol occurred at about 40°C lower than the DSC exothermic transition temperatures (192 and 185°C). Thus, the true optimum molding temperatures could be a few degrees higher or lower than 150 or 140°C, but they would not be detected because of the limitation of temperature control accuracy (\pm 5°C)

of the equipment employed. The relationship between curing quality and curing temperature is further discussed by Sun et al.²⁹

CONCLUSION

Molding temperature, pressure, and time are three major factors affecting the curing quality of

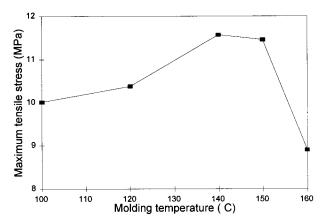


Figure 8 Maximum curing quality of soy protein isolate (SPI) plastics in the presence of 25% glycerol: effects of molding temperature on maximum stress of the SPI plastics molded at 20 MPa. Molding times were 10, 10, 5, 5, and 3 min for molding temperatures of 100, 120, 140, 150, and 160°C, respectively.

soy protein polymers. Water resistance increased as molding temperature and time increased. At low molding pressure the curing quality (i.e., strength, strain, and water resistance) increased as molding pressure increased to 20 MPa, and then decreased slightly as pressure continued to increase. At fixed pressure the molding temperature and time had significant interactive effects on curing quality. At high temperature, for example, at 150°C, it took about 3 min to reach optimum curing quality; however, at low temperature (120°C) it took about 10 min to reach optimum curing quality. The maximum strength and strain of the cured protein polymer occurred at the molding temperature close to its phase transition temperature or about 40°C below its exothermic temperature.

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