Properties of Molded Soy Protein Isolate Plastics

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ABSTRACT: Thermal property of soy protein isolates (SPI) was studied with differential scanning calorimetry and thermogravimetric analysis. The weight loss of pure SPI is about 300°C. The glass transition temperature (T_g) is above 200°C. The best molding temperature of glycerin plasticized SPI plastics were then given. It is between 125 and 140°C. Subsequently the special property of molded SPI plastics was investigated. Results show that the atmosphere humidity affects the mechanical property and thermal property of SPI plastics. With the increasing humidity, the tensile strength decreases. While the elongation at breakage and peak area of the differential scanning calorimetry curve increases. At high temperature even at 140°C the molding temperature SPI plastics still have tensile strength though it decreases with the increasing test temperature while elongation at breakage increases. Dynamic mechanic thermal analysis test show that the storage modulus decreases with the rising temperature. The mechanical loss peak appears at lower temperature with the increasing amount of glycerin content. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3716–3720, 2007

Key words: soy protein; plastics; property; biodegradability; mold; DMTA

INTRODUCTION

Today's plastics are designed with little consideration for their ultimate disposability or the effect of the resources used in making them. This has resulted in mounting worldwide concerns over the environmental consequences of such materials when they enter the mainstream after their intended uses. This led to the concept of designing and engineering new biodegradable materials—materials that have performance characteristics of today's materials but that undergo biodegradation along with other organic waste to soil humic materials. Hence the production of biodegradable materials from annually renewable agricultural feedstock has attached attention in recent years. Agriculture materials such as starches and proteins are biodegradable and environmentally friendly. Soybean is a good candidate for manufacturing a large number of chemicals, including biodegradable plastics.

Soy protein is relatively low cost with vast available supplies. Commercially available soy protein products include soy protein isolate (SPI), soy protein concentrate, and soy flour. SPI, prepared by precipitation at pH 4.5, consists of more than 90% protein, whereas soy protein concentrate, prepared by eluting soluble components from defatted soy flour, contains more than 70% protein and about 18% carbohydrate. Soy flour contains about 56% protein and about 34% carbohydrate. Approximately 90% of the proteins in soybeans are dehydrated storage proteins. Major components in the storage proteins are conglycinin (7S) (35%) and glycinin (11S) (52%). Both 7S and 11S proteins are of quaternary structures. The 7S protein has nine subunits with an average molecular weight of 100,000–200,000, whereas the 11S has three acidic and three basic subunits of ~350,000 and 600,000, respectively.

Patents for soy protein plastics were early published in France's and England's patents in 1913, respectively. By 1930 the impending Great Depression forced Henry Ford to look for ways to increase farm income to protect farm-related purchases of his automobiles.[1] Since 1950s, great progress was made in petroleum chemical technology, and the petroleum-based plastics dominate today's plastics market because of their high strength, lightweight, low cost, easy processability, and good water barrier properties. In the last decade of the 20th century, people pay much more attention to the environment and renewable resources. This formed the great driven force, which leads to develop a new kind of biodegradable green plastics using renewable natural polymers including soy proteins.

Jane and coworkers[2] studied the effects of pH, moisture content, processing conditions, crosslinking agents, and cellulose (as filler) on mechanical and physical properties of compression-molded soy plastics,[3] and the morphology and biodegradation of the soy protein-based plastics.[4] Effects of polyhydric

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alcohols as plasticizers on mechanical properties of soy protein-based plastics had also been studied and reported.[5] Otaigbe and Adams[6] studied the composite of soy protein with polyphosphate, and their results showed enhanced strength, stiffness, and improved water resistance.

Sun et al.[7] studied the mechanical, water absorption property, and the fracture morphology of molded samples (molded at 120–175°C) made from 7S, 11S globular and the mixture of them (1 : 1), respectively. More than that they investigated the curing process and mechanical properties of protein-based polymers made from soy proteins after being cured.[8] Zhang et al.[9] studied the mechanical and thermal properties of extruded soy protein sheets.

In this research thermal property of SPI and best molding temperature of SPI plastics were given. Then effects of environment humidity and tensile testing temperature on mechanical and thermal property of SPI plastics were studied. Dynamic mechanical property was investigated by using dynamic mechanic thermal analysis (DMTA).

EXPERIMENTAL

Materials

SPI was purchased from Protein Foodstuff Factory of ShanDong WuCheng Dawang Group, and used as received. It contains more than 89% protein(dry basis), less than 7% moisture and 6.0% ash. Glycerin was reagent grade quality and was purchased from YongHua Special Chemical Reagent Factory of ShangHai. Pure water was obtained from Shandong Agriculture University's Pure Water Factory. Dry Silica gel; $MgCl_2$, $Mg(NO_3)_2$, NaCl reagent (CP) were purchased from Shanghai Chemical Reagent Stock Provider.

Preparation of SPI plastics

SPI, glycerin or other additives were thoroughly milled in a beaker. The mixture was equilibrated overnight in the sealed beaker. Then prepared as following: the mixture was molded in a press (QLB-1D, Huzhou Rubber Machinery Factory, Zhejiang China) (15 MPa) at different temperature for 20 min. Then it is moved to a press at room temperature for cooling. The molding temperature varied from 60 to 160°C.

Dry silica gel and saturated $MgCl_2$, $Mg(NO_3)_2$ and NaCl solutions were put into four desiccators, respectively. The relative environment humidity inside each desiccators are 0, 32%, 50 and 75%, respectively. The samples were hung in them for 7 days after dried for 24 h in a vacuum oven at 105°C. The conditioned sample left for test directly.

Thermal analysis

Differential scanning calorimetry (DSC) was used to determine the T_g of SPI. Approximately, 5 mg sample was analyzed using Perkin–Elmer Pyris1 Seris. Temperature ranges from 50 to 250°C, heating rate 20°C/min. Nitrogen gas flow at 30 mL/min. Thermogravimetric analysis (TGA) curve was obtained by using Perkin–Elmer TGA7. Temperature ranges from 50 to 800°C. Heating rate is at 20°C/min. Nitrogen gas flow at 50 mL/min. All used platinum pan.

Mechanical properties

The molded sheets were cut into dumbbell shape according to China GB1040-1992, type III. Specimens were preconditioned at 23°C, 50% relative humidity for 48 h. Mechanical properties were measured using an Instron Universal Test Machine (Model 4465). The crosshead speed was 50 mm/min. Stress–strain curves were recorded. Tensile strength, elongation at break (percent) and Young's modulus were obtained from the test. The values presented are averages of five samples.[10]

Moisture content measurement

Moisture content measurement was conducted using Fast moisture Content Measurement (SC69-02, Shanghai the Secondary Balance Instrument Factory). Scissor the sample into smash before put into the instrument. Weight W_1. Then warm up for 30 min. Weight W_2. Moisture content was calculated as follows: $(W_1 - W_2)/W_1 \times 100\%$.

Gel content test

100 hole/in. copper net (W_1). SPI plastics sample dehydrated in 50°C vacuum oven till constant was put into the former copper net (W_2). Immersed in pH = 13 solution for 24 h. Dried in 50°C vacuum oven until the weight is a constant W_3. Gel content is calculated as follows: $(W_3 - W_1)/(W_2 - W_1) \times 100\%$.

Tensile test at high temperature

Tensile test at given temperature referring to China Standard GB1040-1992 Tensile Test for plastics III type in constant temperature oven of Instron Materials Test Machine. Specimens were preconditioned at 23°C 50% relative humidity for 48 h. Then put onto the clips in the oven at constant temperature for 2 min. The crosshead speed is 50 mm/min. Stress–strain curve were recorded. Tensile strength at maximum load, elongation at break were calculated. The reported values are means of five samples.

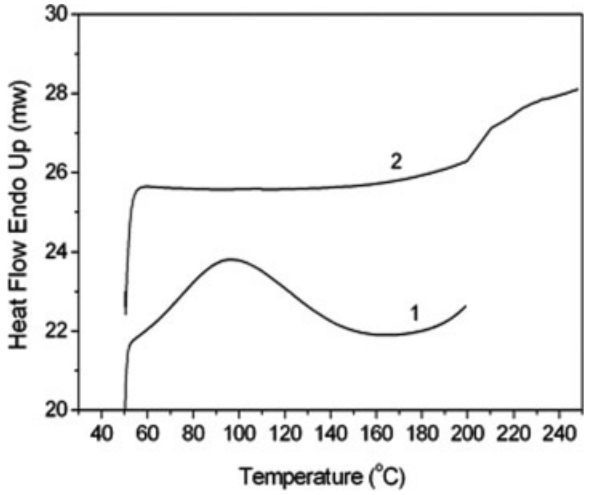

Figure 1 DSC thermogram for SPI rising temperature for the 1-first time; 2-s time.

DMTA test

Rectangular samples of the plasticized materials (20 $\times$ 4 $\times$ 1 mm^3) were analyzed with a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific, USA) equipped with a cryogenic system fed with liquid nitrogen. A single cantilever bending test was performed with a temperature range from -50 to 150°C at a heating rate 3°C/min. A variable sinusoidal mechanical stress was applied to the sample (frequency = 10 Hz) to produce a sinusoidal strain amplitude of 0.016%. A continuous flow of nitrogen gas in the oven provides an inert atmosphere. During analysis, the storage modulus (E'), the loss modulus (E'') and tan δ ($=E''/E'$) were recorded and plotted against temperature for further evaluation of thermal transition.

RESULTS AND DISCUSSION

Thermal property of pure SPI

DSC and TGA thermogram were given in Figures. 1 and 2. There is a peak at about 100°C in the DSC curve of rising temperature for the first time. But it is not the melting point of SPI. Actually it is caused by the moisture in the SPI. On the TGA thermogram, it can be seen that there is a weight lose peak below 100°C, which is resulting from the loss of the moisture in the SPI.[9] From the curve of rising temperature for the second time of DSC, there is a transition at about 200°C, which can be attributed to the glass transition point of pure SPI.[8] Also from TGA curve, there is a main weight loss peak at 300°C. The instability of SPI begins at 200°C. That means the processing temperature for SPI plastics can not be higher than 200°C because of its thermal decomposed. So plasticizer or other modifier is needed for the preparation and processing of SPI plastics.

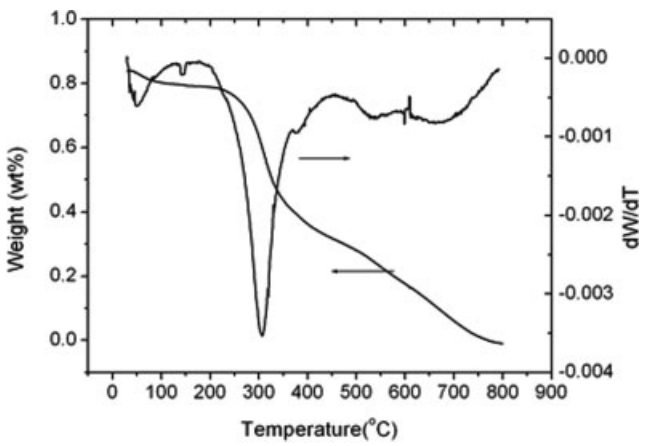

Figure 2 TGA thermogram for SPI.

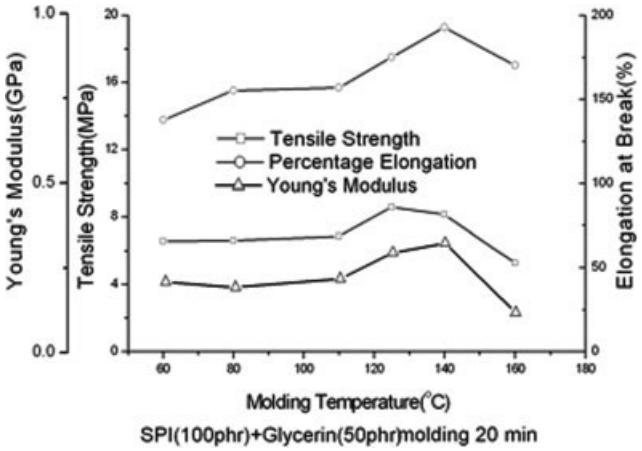

Figure 3 Effect of molding temperature on the mechanical property of glycerin plasticized SPI plastics.

Best molding temperature for SPI plastics

Mechanical property of the molded sheets of glycerin plasticized SPI at different temperature for 20 min is given in Figure 3. It can be seen that at 60°C the blend can be molded into sheet, and the sample already has its tensile strength and elongation at break. When the temperature is risen to 125°C, both tensile strength (including Young's Modulus) and elongation at break increase. 125–140°C are the best molding temperature. When the temperature is risen to 160°C, tensile strength and elongation at break decrease, it may be caused by the degradation of protein.

Effect of environment humidity on mechanical property, moisture content, and thermal property of SPI plastics

Stress–strain curve, moisture contents and the DSC curve of the samples conditioned at 0, 32%, 50 and 75% relative humidity environment for 7 days were given in Figures 4 and 5; Table I.

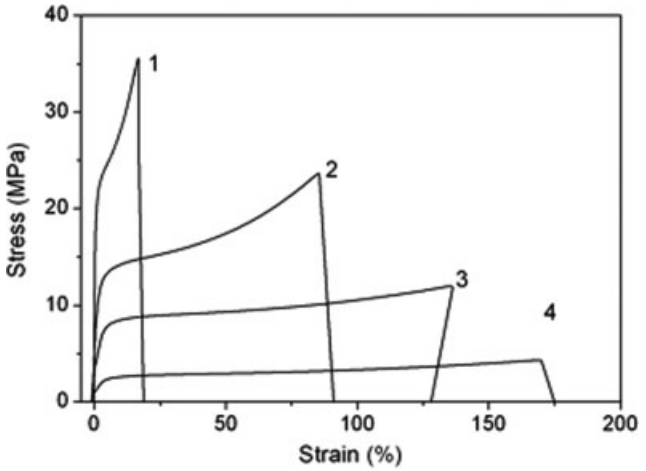

Figure 4 Effect of environment humidity on the stress–strain curve of SPI plastics molded directly: 30 phr glycerin, conditioned in the relative humidity at 0, 32, 50, 75% for 1 week for curve 1, 2, 3, 4.

The results show that with the increasing of the conditioned environment humidity SPI plastics changed from rigid and brittleness to soft and toughness plastics. Higher the environment humidity is, smaller the tensile strength and longer the elongation at breakage of the conditioned SPI plastics are. Moisture contents of the conditioned SPI plastics increased with the conditioning environment humidity. There existed heat absorption peaks at about 100°C in the DSC curve of SPI plastics. The peak area increased with the moisture content of the SPI plastics conditioned with the increasing environment humidity.

Tensile property of SPI plastics tested at high temperature

Gel content of the SPI plastics influenced by the molding temperature is given in Table II. It can be seen that with the increasing of the molding temperature, more complete gelatin of the protein molecule happened.[11]

When molding temperature is higher than 110°C, gelatin happened in the protein molecule. And the gel content can be detected. The gelatin is the cross-link between protein molecules. This may affect the mechanical property of SPI plastics especially the tensile property at high temperature, even at or more than the molding temperature. Results in Figure 6 show that tensile strength decreased with the increasing tested temperature and elongation at breakage increased. Also even at the molded temperature 140°C SPI plastics has tensile strength, which can be tested out. This indicated that there existed gel in SPI plastics, which did not melt and dissolve.

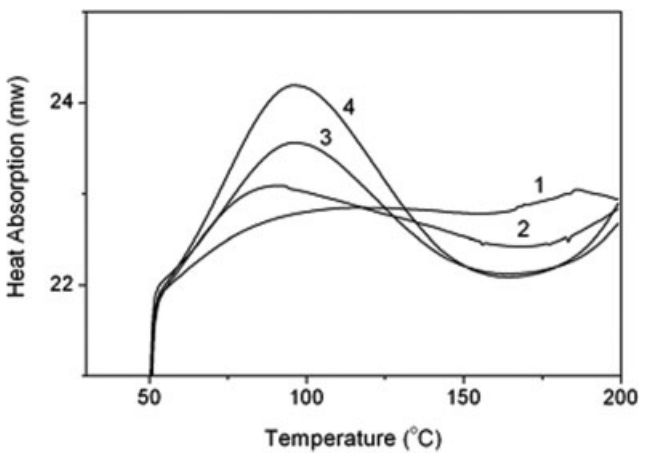

Figure 5 Effect of environment humidity on the DSC curve of SPI plastics conditioned in the relative humidity environment of 0, 32, 50, 75% for 1 week for curve 1, 2, 3, 4.

TABLE I
Moisture Contents of the Samples Conditioned in Different Relative Humidity Environment

Relative humidity (%)	Moisture contents (%)
0	2.0
32	4.5
50	7.9
75	15.2

Dynamic mechanical property of SPI plastics

DMTA is very sensitive to the changes in molecular motions and interactions occurring over the transition region, this technique was used to study the glass transition of the series of sample. Typical DMTA scans of SPI plastics were shown in Figures. 7 and 8.

It can be seen that the storage modulus decreased with the glycerin contents at the same temperature. With the increasing temperature storage modulus decreased (Fig. 7). Peak in tan δ is mechanical loss peak indicates the glass transition temperature of SPI plastics. With the increasing glycerin contents the peaks move to lower temperature. Wide tan δ peak means protein molecular movement is complex.

TABLE II
Effect of Molding Temperature on Gel Content of the SPI Plastics

Molding temperature (°C)	Gel content (%)
60	0
80	0
110	3.5
125	20.2
140	27.6
160	43.5

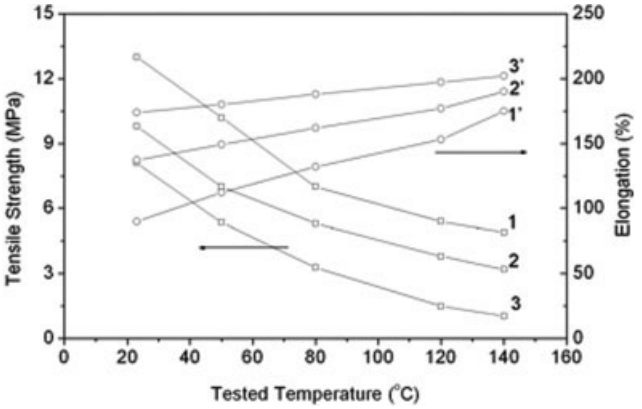

Figure 6 Mechanical property of molded SPI plastics tested at different temperature curve 1, 2, 3 stand for 30, 40, 50 phr glycerin plasticized SPI plastics, molded at: 140°C × 20 min.

CONCLUSIONS

Glass transition temperature (T_g) for SPI is about 200°C. The mechanical property of glycerin plasticized SPI plastics enhances with the rising molding temperature. 125–140°C is the best molding temperature. It decreases if the molding temperature is risen higher than 140°C. Environment humidity affects the mechanical and thermal properties of soy protein plastics. With the increasing humidity, tensile strength decreases and the elongation at breakage and the peak area of the DSC curve increases. The tensile strength decreases with increasing tested temperature, and it can be detected at high temperature, even at 140°C the molding temperature for SPI plastics. Gelatin happened at about 110°C for soy protein. Gel contents of SPI plastics increased with higher molding temperature. The storage modulus decreases with the temperature rising. The mechanical loss peak appears at lower temperature with the increasing amount of glycerin content.

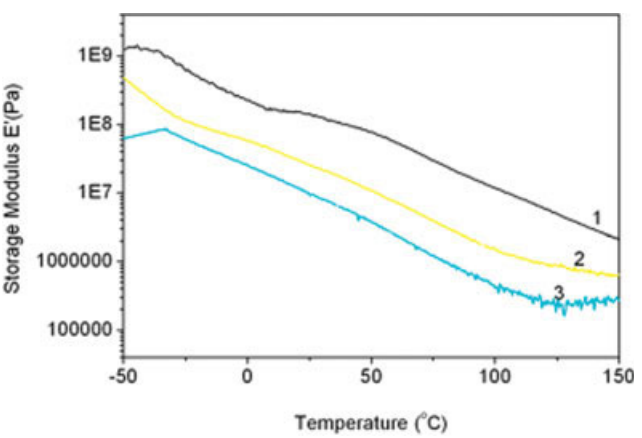

Figure 7 Storage modulus of molded SPI plastics as a function of temperature at different glycerin contents the glycerin contents are 20, 40, 50 phr for curve 1, 2, 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

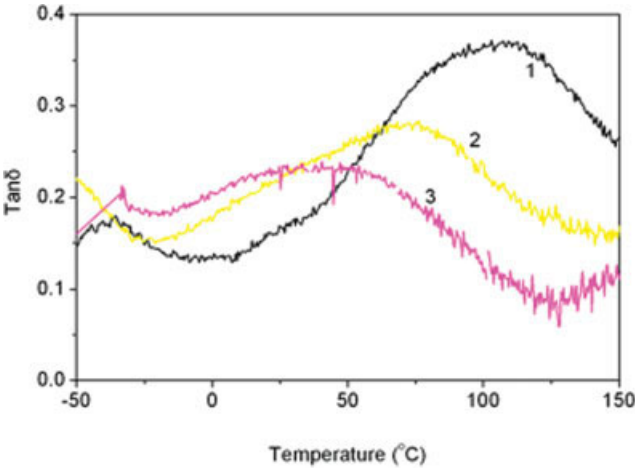

Figure 8 Tan δ of molded SPI plastics as a function of temperature at different glycerin contents the glycerin contents are 20, 40, 50 phr for curve 1, 2, 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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