

Structure and Properties of Soy Protein Films Plasticized with Hydroxyamine

Huafeng Tian,¹ Dagang Liu,^{1,2} Lina Zhang¹

¹Department of Chemistry, Wuhan University, Wuhan 430072, China

²College of Forestry, South China Agricultural University, Guangzhou 510642, China

Received 30 September 2007; accepted 23 July 2008

DOI 10.1002/app.29160

Published online 30 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two kinds of transparent films of soy protein were successfully prepared by plasticizing with diethanolamine (DEA) and triethanolamine (TEA). The films were hot pressed at 140°C and 20 MPa, and characterized with Fourier transform infrared spectroscopy, scanning electron microscope, ultraviolet–visible spectrometer, differential scanning calorimetry (DSC), thermogravimetric analysis, and tensile testing. The results indicated that films with triethanolamine plasticizers possessed better optical transmittance (more than 80% at 800 nm) than those with diethanolamine and glycerol. All of the sheets exhibited only one T_g in DSC

curves. Moreover, the soy protein plastics with TEA had higher thermal stability and mechanical properties, as well as lower water uptake than those with DEA and glycerol, as a result of the strong interaction between TEA and protein molecules. The soy protein materials will be promising for the application in the fields of package and container, substituting for the nongreen polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1549–1556, 2009

Key words: soy protein; hydroxyamine; plasticization; green materials

INTRODUCTION

Because of concerns of the environmental crisis caused by petroleum-based nondegradable materials and the impending petroleum finite resources, degradable polymers based on natural renewable resources are attracting more and more attentions now.^{1–7} Natural polymers mainly include cellulous, starch, protein, chitin, lignin, etc., which have a wide source and could be biodegraded to CO₂, water, and other organic small molecules by microorganisms in natural environment and alleviate the environmental problems.⁸ Soybean protein, the coproduct of the soybean oil industry, is readily available from renewable resources and agricultural processing industry. Plastics from soy protein could be totally degraded in humid environments by microorganisms. In the past decade, soy protein-based “green” materials have become a research focus because of their low cost and eco-friendly characteristics.^{1,3,4,7} Moreover, the costliness of petro-

leum promoted the development of protein-based materials then. Recently, with the increasing petroleum cost and severe environmental pollution, the research on protein plastics has attracted much attention.

Soy protein has been considered as a potential substitute for synthetic petroleum polymers in the applications of plastics, adhesives and so on.⁹ Soy protein isolate (SPI) has a protein content of more than 90%, and consists of about 18 kinds of amino acids,¹⁰ of which about 62% are polar and reactive amino acid residues.¹¹ Pure soy protein plastics without any additives often have a brittle property and have a processing temperature around 200°C near its decomposition, which makes the difficult processing.¹² Addition of plasticizers is an effective way to obtain a flexible proteineous plastic. Glycerol is regarded as one of the most effective plasticizers. The –OH groups of glycerol could interact with –NH₂, –NH–, –COOH, etc., therefore decrease the inter- and intramolecular interactions such as hydrogen bond and improve the motion ability of protein macromolecules, which results in the flexibility of materials. Glycerol (25 wt %) could reduce glass transition temperature (T_g) from about 150°C of soy protein without plasticizer to –50°C determined by dynamic mechanical thermal analysis.⁷ The disadvantages of glycerol plasticizer are moisture sensitivity and time-dependent properties resulted from leaching out of plasticizers over time.¹³ Soy protein plastics could absorb moisture in the atmosphere,

Correspondence to: L. Zhang (lnzhang@public.wh.hb.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 59933070, 20474048.

Contract grant sponsor: Key Laboratory of Cellulose Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences.

which could reduce the tensile strength and modulus sharply.

In response to problems of high hydrophilicity and low-thermal stability, it is possible to replace glycerol with a higher molecular weight compound with hydrophobic subsistent. Recently, in our laboratory, a kind of amide plasticizers has been used to plasticize soy protein materials.^{14,15} The structure and polar similarity between amide and protein molecules lead to a good compatibility between the two materials.

Compounds with amino or imine functional groups and hydroxyl functional may be also good plasticizers for soy protein due to the good compatibility between these groups and soy protein molecules. Hydroxyamines have been used as plasticizers for wheat gluten¹⁶ and achieved good results. However until now, soy protein plastics plasticized by hydroxyamines have been reported scarcely. The aim of this work mainly investigates the effect of the plasticizers with different molecular weight [diethanolamine (DEA) and triethanolamine (TEA)] on structure and properties of the resulted soy protein plastics. Their structure and properties were characterized with Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), ultraviolet-visible spectrometer (UV), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile tests. This work provides important information of new plasticizers for SPI for the research and development of these biomaterials.

EXPERIMENTAL

Materials

Commercial SPI was purchased from Dupont-Yunmeng Protein Technology Co. Ltd. (Yunmeng, China). The weight-average molecular weight (M_w) of SPI was determined by multiangle laser light scattering instrument (MALLS, DAWN (DSP, Wyatt Technology Co., USA) equipped with a He-Ne laser ($\lambda = 632.8\text{nm}$) to be 2.05×10^5 (g mol^{-1}).¹⁷ DEA was of chemical grade and purchased from Chemical Reagent Co. of National Medicine Group. TEA and glycerol were all of analytical grade and purchased from the Shanghai Chemical Co. (Shanghai, China) and first Shanghai Chemical Reagent Co. (Shanghai, China), respectively. The main physical and chemical properties of the three plasticizers are given in Table I. Each molecule of DEA or TEA has three active units to form hydrogen bond with protein molecules. It is worth noting that ethanolamine with the similar structure with DEA and TEA was not examined due to its pungent odor like ammonia, which prevents it to be used as a plasticizer. All

TABLE I
Main Chemical and Physical Properties of the Plasticizers Used in This Work

	Diethanolamine	Triethanolamine
Carbon number	4	6
Molecular weight	105	149
Active units to form		
H bonds per molecule	3	3
Density (g cm^{-3})	1.097	1.124
Melting point ($^{\circ}\text{C}$)	19.8	22.3
Boiling point ($^{\circ}\text{C}$)	268.8	360.0
T_g ($^{\circ}\text{C}$)	-79.7	-67.0

materials were kept in desiccators with P_2O_5 as desiccant during experiment period.

Preparation of samples

SPI with desired plasticizer content was mixed in a mortar for 1–2 h. The resulting mixtures were equilibrated in a little sealed glass bottles at 5°C for 24 h. Subsequently, each mixture was placed in a mold covered with two polished stainless steel plates and compression-molded at 140°C under the pressure of 20 MPa for 10 min. Then, the sheets were air cooled to room temperature under constant pressure with the cooling rate of about $3^{\circ}\text{C min}^{-1}$ before the removal from the mold. The sheets plasticized with 10–50 phr (percent mass ratio of the plasticizer to SPI) plasticizers were coded as SD (ST) 10–50, where SD and ST represented sheets with DEA and TEA, respectively. Control samples with 30 phr glycerol were also prepared, coded with SG30. All of the sheets were vacuum dried at 50°C until a constant weight and then conditioned in desiccators with P_2O_5 as desiccant before testing.

Characterization

The kinetics of water absorption and the water uptake (WU) of all the samples were determined by conditioning the samples at room temperature in a desiccator containing saturated NaCl solution to provide a relative humidity (RH) of 75%. Sheets with rectangular dimensions of $50\text{ mm} \times 10\text{ mm} \times 0.1 \sim 0.3\text{ mm}$ were removed from the desiccator at specific intervals and weighed on a five-digit balance. The film thickness was supposed to be thin enough so that the water molecular diffusion was considered one dimensional. The water content or WU of the sheets was calculated as¹⁸

$$\text{WU}(\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

where M_t and M_0 are the weight of the sample after exposure to 75% RH for t min and the initial weight of the sample at 0% RH, respectively. Samples were

conditioned for at least 300 h to reach equilibrium. The water diffusion coefficient D was also calculated, and the details of the calculation can be found elsewhere.¹⁸

Film opacity was determined using a procedure described by Gontard et al.¹⁹ with a little modification. The percent optical transmittance (Tr) of the sheets (where $Tr + \text{absorbance } (Ar) = 100\%$) was measured with an ultraviolet–visible spectrometer (UV-160A, Shimadzu, Japan). A rectangle sheet (4 cm \times 1 cm) was placed on the internal side of a spectrophotometer cell, and the transmittance/absorbance spectrum was recorded for each sample in the wavelength range from 800 nm to 400 nm (the transparency of all the sheets tends to be zero when the wavelength is less than 400 nm). Film opacity was defined as the area under the recorded absorbance curve and determined by integration. The opacity was expressed as absorbance units \times nanometers ($AU \times \text{nm}$), and the specific opacity was calculated by

$$\text{Specific opacity} = \frac{Au \times \text{nm}}{d} \quad (2)$$

where d is the thickness of the samples. The final values of opacity expressed in this article were values compared with ST40 when the specific opacity value of ST40 was normalized at 1.

Fourier transform infrared spectra of the samples were carried out on a Nicolet 5700 FTIR spectrometer (Thermo Electron Co., USA) in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1} using the KBr-disk method. Scanning electron microscopy images were taken on an S-570 microscope (Hitachi, Japan). The dry sheets were frozen in liquid nitrogen and snapped immediately, and then, the cross section faces of the sheets were coated with gold for SEM observations.

DSC was carried out on a Diamond DSC apparatus (Perkin–Elmer Co., USA) equipped with a cooler system with liquid nitrogen. Dry power sample (about 10 mg) was placed in pressure-tight aluminum DSC cells under nitrogen atmosphere and maintained at 100°C for 5 min to eliminate residual water in the sample. Then, the sample was quenched to –100°C, and then heated to 250°C under nitrogen atmosphere with a heating rate of 10°C min^{-1} . The glass transition temperature (T_g) was taken as the midpoint of the specific heat increment at the glass–rubber transition. TGA was carried out on a Pyris TGA linked to a Pyris diamond TA lab system (Perkin–Elmer Co., USA) at a heating rate of 10°C min^{-1} between 25°C and 500°C under nitrogen atmospheres. The mass of the samples was ~ 5 mg.

The tensile strength (σ_b), elongation at break (ϵ_b), and Young's modulus (E) of the sheets were measured on a universal testing machine (CMT6503,

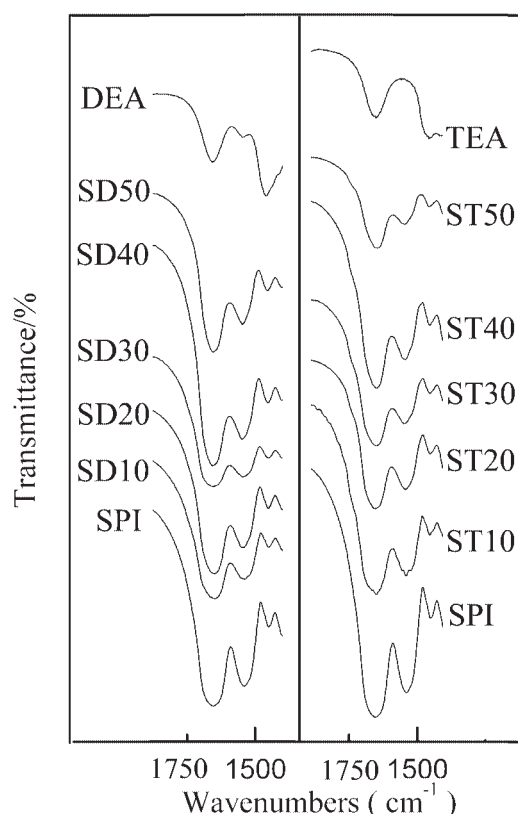


Figure 1 FTIR spectra at 1800 \sim 1400 cm^{-1} for the SD (a) and ST (b) sheets.

Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) with a tensile rate of 5 mm min^{-1} according to ISO 527-3: 1995 (E) at room temperature. An average value of five replicates of each sample was taken. All the samples were conditioned under 75% RH to get a constant weight before mechanical testing.

RESULTS AND DISCUSSION

Structure and compatibility of plasticized soy protein

FTIR spectra for the SD and ST sheets are shown in Figure 1. The peaks around 1656 cm^{-1} and 1541 cm^{-1} were attributed to the characteristic amide bands: amide I (C=O stretching), amide II (N–H bending and C–N stretching),^{20,21} respectively. Compared with the amide bands of pure soy protein, the bands of the amide I and amide II for SD and ST became a little multiple, especially for SD10 and ST10, which indicated the existence of hydrogen bonds between the soy protein peptides and the polar groups of the plasticizers.³

The transparency or opacity of materials can be used to judge the compatibility and homogeneity of blends.^{21,22} Figure 2 shows the dependence of optical transmittance on plasticizer content of different soy

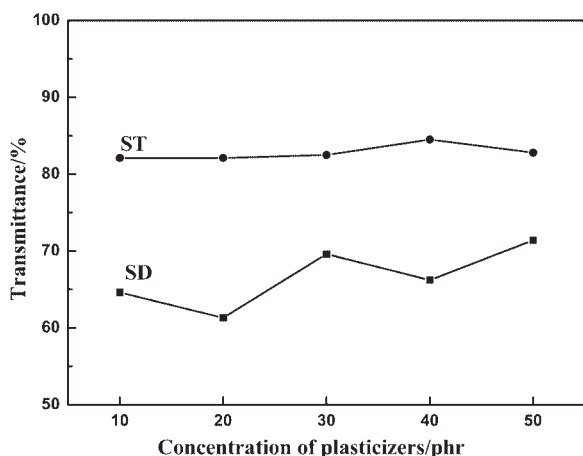


Figure 2 Optical transmittance of the SD and ST sheets at 800 nm.

protein series at 800 nm. SD10 and ST10 were not tested because they were too brittle to handle. All the sheets exhibited good transmittance at 800 nm, which was 64 ~ 72% for the SD series and 82 ~ 85% for the ST series. Moreover, the optical transmittance of ST was better than that of SD. Interestingly, the ST sheets showed even better transparency than soy protein plastics plasticized with acetamide and glycerol (below 80% at 800 nm).¹⁴ The specific opacity of the two series of plastics and pictures of the SD30 and ST40 sheets are displayed in Figure 3. The specific opacity of ST40 was set as 1. The values of opacity were related to the kind of the plasticizer. SD30 and ST40 exhibited lower opacity or the higher transparency than others, and the ST40 sheet was more transparent than SD30. Homogenous structures of soy protein plastics were achieved when 30 phr DEA or 40 phr TEA were added, indicating a good compatibility with soy protein. Clearly, the ST sheets were more transparent than the SD series.

Figure 4 displays the SEM micrographs of fractured surfaces (cross section) of different samples. Nonhomogenous surfaces appeared at lower concentration of plasticizers, which could be attributed to low amount of plasticizer. At higher plasticizer content (30–40%), the fracture surfaces exhibited almost homogeneous structure. However, further addition of plasticizers, extra amount of plasticizers again gave a nonhomogeneous surface. In view of the results, the hydroxyl groups and imine groups of DEA and TEA could form hydrogen bond with protein macromolecules, leading to a good compatibility.

Thermal properties

Figure 5 shows the DSC thermograms of the SD and ST sheets. For thermograms of pure TEA, the exothermal peak at -17.4°C was attributed to crystalli-

zation (T_c) of TEA. The endothermal peak at about 22.3°C was attributed to melting (T_m) of TEA. The glass transition temperature (T_g) of TEA was -67.0°C . Those values of T_c , T_m , and T_g for DEA were -19.3°C , 19.8°C , and -79.7°C , respectively. The T_m and T_c peaks have disappeared in DSC thermograms of both the SD and ST sheets, indicating that hydroxyamine plasticizers were dispersed in soy protein plastics homogeneously as a result of the strong interaction between the plasticizers and protein molecules, leading to the good compatibility of these materials. All the SD and ST sheets exhibited a broad endothermal peak at about $215 \sim 220^{\circ}\text{C}$, attributed to the denaturation of soy protein. The pure SPI powder has a denaturation temperature (T_n) at 155°C .²³

TEA has three $-\text{O}-\text{H}$ groups, and DEA molecule has two $-\text{O}-\text{H}$ groups and one $-\text{N}-\text{H}$ group in their structure. Both the $-\text{O}-\text{H}$ and $-\text{N}-\text{H}$ could easily form hydrogen bond with $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{NH}$ of the protein,⁴ leading to the breaking of the hydrogen bond between protein chains. Although glycerol plasticized soy protein plastics

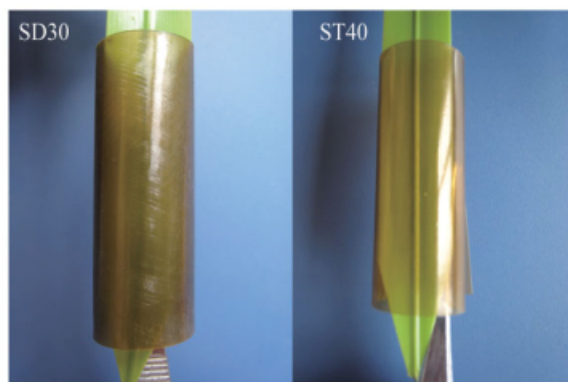
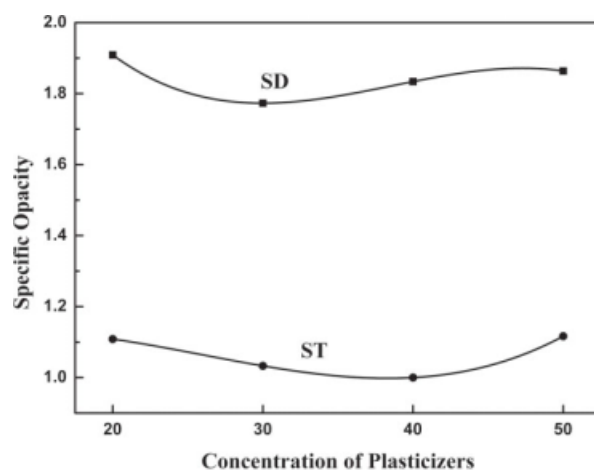


Figure 3 Specific opacity of soy protein based plastics with different plasticizers (top) and the transparent films of SD30 and ST40 (bottom). The specific opacity value of ST40 was normalized at 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

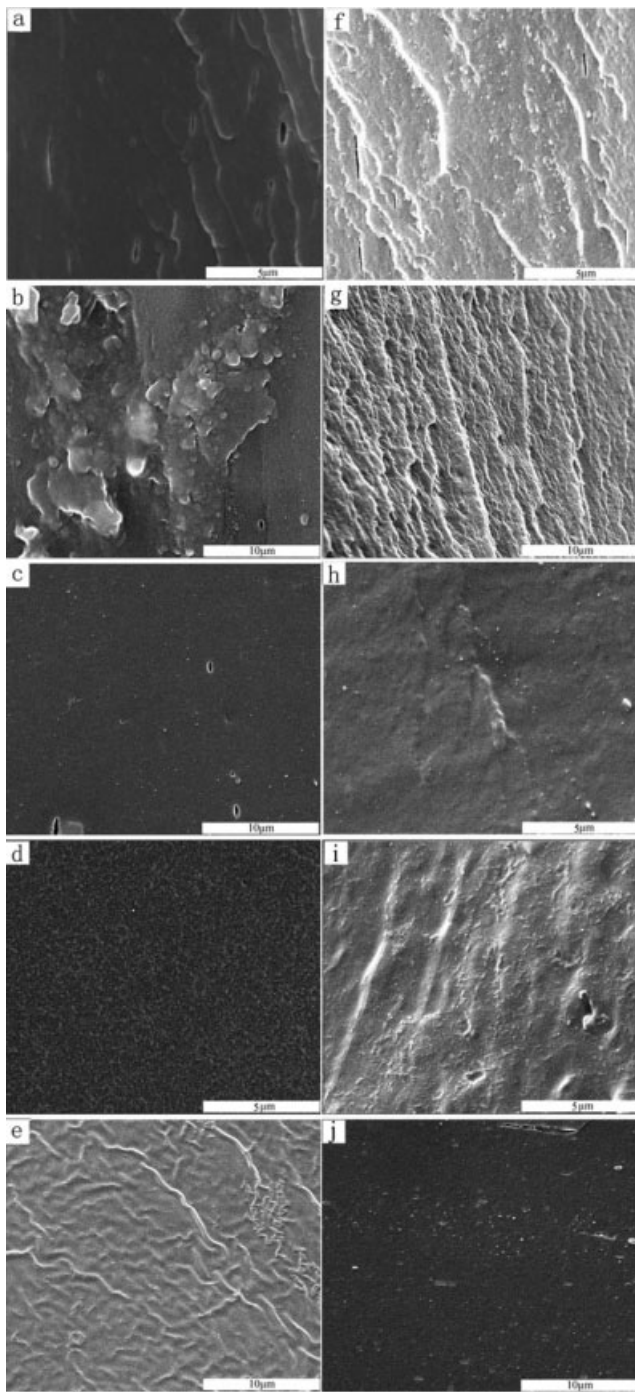


Figure 4 Scanning electron micrographs of the cryo-fractured surfaces of (a–e) for SD10 ~ SD50 and (f–j) for ST10 ~ ST50.

have two glass–rubber transition temperatures assigned to protein-rich domains and plasticizer-rich domains,²⁴ both the SD and ST sheets exhibited one glass transition temperature, indicating such phase separation could not be observed in the DSC tests. The fine miscibility and low mobility may be responsible for the lack of phase separation and only one T_g . There was a tendency that glass transition temperatures decreased with the increase of plasticizers.

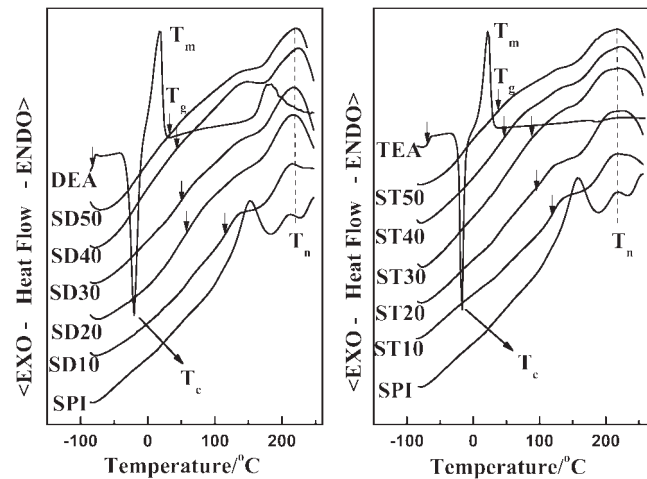


Figure 5 DSC thermalgrams of soy protein plastics with different contents of DEA and TEA at RH = 0%.

Compared with the SD sheets, the ST sheets had a higher T_g . Soy protein plastics plasticized with glycerol has T_g of below 0°C,²⁴ which was even lower than the SD sheets. On the whole, as the molecular weight of plasticizers (glycerol, DEA, and TEA) increased, the glass transition temperature of the protein plastics was enhanced.

The TG thermograms of the SD and ST sheets are displayed in Figure 6. Usually, the thermal degradation behavior of SPI consists of two steps: the evaporation of residual moisture (from room temperature to about 150°C) and the degradation of soy protein (above 150°C).¹⁴ In this work, the evaporation of residual moisture and plasticizers in the SD and ST sheets occurred at 100 ~ 250°C, and the degradation of soy protein appeared at 250 ~ 400°C. The

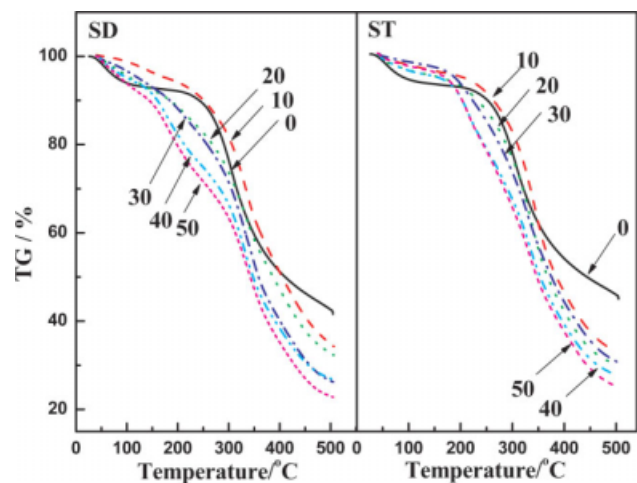


Figure 6 TG curves of the SD and ST series at RH = 0% under N_2 atmosphere. The plasticizer content (phr) was marked in the figure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

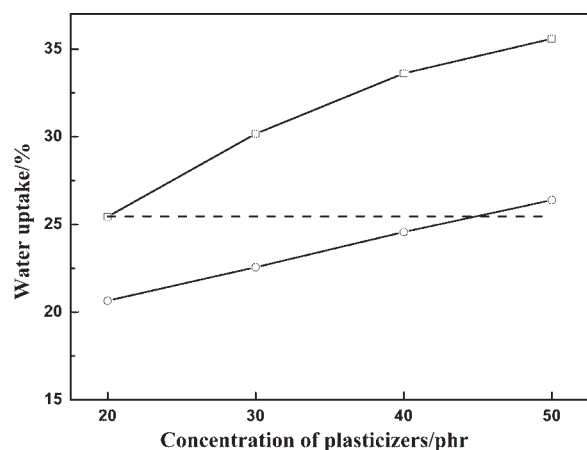


Figure 7 Equilibrium water uptake of samples conditioned at RH = 75% as a function of the content of DEA (□) and TEA (○). The dashed line demonstrates the water uptake of SG30 samples.

temperature at the peak around 250 ~ 400°C (T_{max}) of the DTG curves (not shown) corresponds to the maximum decomposition rate of soy protein, and the weight loss in this temperature was almost the same, about 40 ~ 50%. All the SD and ST sheets had a higher T_{max} than SPI, indicating a relatively higher stability. For SD and ST, the maximum weight loss rate reflecting the decomposition of soy protein appeared at about 250 ~ 400°C, whereas glycerol-plasticized soy protein plastics had a maximum rate at around 200°C.²⁴ Furthermore, the glycerol-plasticized protein plastics had a much larger weight loss during the temperature range with the escape of plasticizers, which indicated that DEA and TEA possessed a stronger affinity with soy protein macromolecules. The temperature of maximum weight loss rate resulted from plasticizers escape of the ST

sheets was higher than that of the SD sheets. The thermal stability of the ST sheets was higher than that of SD and SG.

Hygroscopicity and mechanical properties

Equilibrium WU of soy protein plastics with different plasticizers under 75% RH is shown in Figure 7. The kinetics of absorption was relatively fast from initial time to about 70 h and then slowed down and led to a plateau corresponding to the equilibrium of the WU. The WU at equilibrium increased from 25.44% to 35.59% with an increase of the DEA content from 20 to 50 phr and from 20.65% to 26.39% with an increase of the TEA content from 20 to 50 phr, compared with 25.46% for the SG sheets. The WU became higher when plasticizers were added to the soy protein. However, the ST sheets had a lower uptake than the SD and SG sheets. There are more carbon atoms on the backbone of TEA compared with glycerol which results in the higher hydrophobicity of the resulted soy protein plastics. The SD sheets had a higher WU than the SG sheets although the DEA molecule has more carbon atoms compared with glycerol, which might be attributed to the more hygroscopic nature of —NH than —OH group.

Table II displays the water diffusion coefficients (D) of different sheets. With an increase of hydroxylamine plasticizers from 20 to 50 phr, the D values increased from 1.34 to $4.87 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for the SD series or 0.799 to $2.59 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for the ST series compared with $3.40 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for SG30 sheets. Interestingly, the ST sheets had much lower diffusion coefficients than the SD and SG sheets with the same content of plasticizers. This suggested that the ST sheets had hydrophobic nature and the

TABLE II
Water Diffusion Coefficients (D) and Compositions of the Soy Protein Plastics Conditioned at RH = 75%

Sample	D ($\text{cm}^2 \text{ s}^{-1} \times 10^9$)	Soy protein (%) ^a	Hydroxyamine plasticizers (%) ^b	Water (%) ^c	Total plasticizer (%) ^d
SD20	1.34	66.43	13.29	20.28	33.57
SD30	3.75	59.09	17.73	23.18	40.91
SD40	4.09	53.46	21.39	25.15	46.54
SD50	4.87	49.17	24.58	26.25	50.83
ST20	0.799	69.07	13.81	17.12	30.93
ST30	1.97	62.76	18.83	18.41	37.24
ST40	2.24	57.34	22.94	19.72	42.66
ST50	2.59	52.75	26.37	20.88	47.25

^a Expressed on wet basis [(soy protein)/(soy protein + hydroxyamine plasticizers + water)].

^b Expressed on wet basis [(hydroxyamine plasticizers)/(soy protein + hydroxyamine plasticizers + water)].

^c Expressed on wet basis [(water)/(soy protein + hydroxyamine plasticizers + water)].

^d Expressed on wet basis [(hydroxyamine plasticizers + water)/(soy protein + hydroxyamine plasticizers + water)].

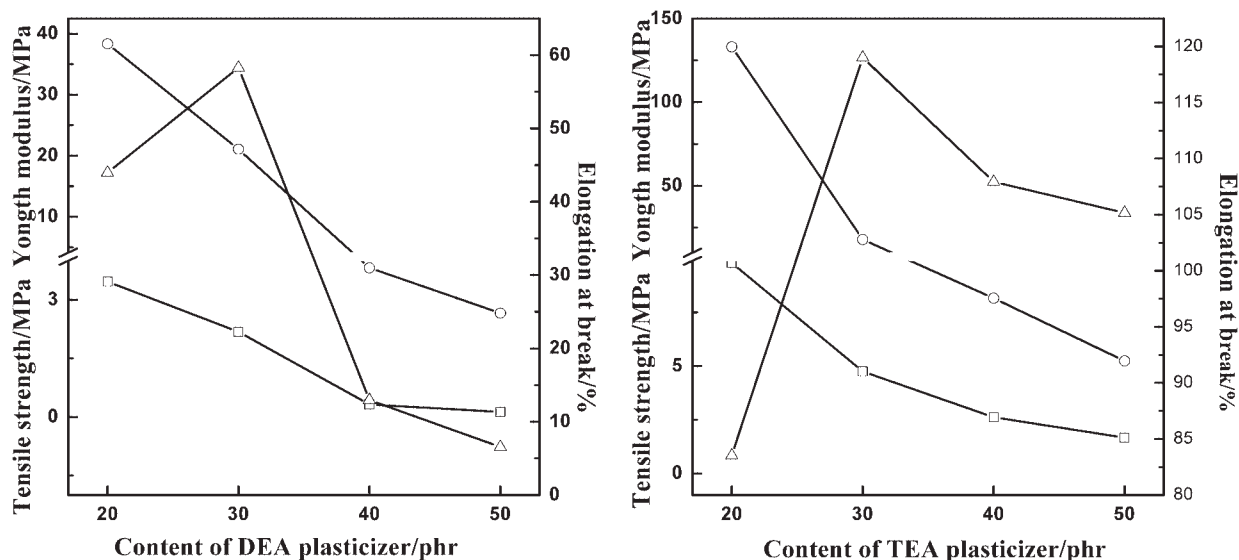


Figure 8 Tensile strength (\square), elongation at break (Δ), and Young's modulus (\circ) of soy protein plastics with DEA and TEA as plasticizers at RH = 75%.

compact structure, compared with DEA and glycerol.

Figure 8 shows the mechanical properties of the soy protein based plastics conditioned at RH = 75%, and the detailed compositions are also displayed in Table II. For both the SD and ST sheets, the tensile strength and Young's modulus dropped with an increase of DEA or TEA, whereas the elongation at break increased rapidly to the maximum value at the plasticizer concentration of 30% phr and then decreased with further increase of plasticizers. TEA-plasticized plastics had a better mechanical performance than DEA-plasticized plastics. From Table II, we could conclude that water may affect the SD plastics more than ST series, namely more water than hydroxyamine plasticizers in the SD series. The content of total plasticizers (water + hydroxyamine plasticizer) increased with the increase of hydroxyamine plasticizer, whereas the SD series had higher total plasticizer content than ST with the same content of hydroxyamine plasticizer. DEA had a best compatibility when 30 phr was added, leading to the maximum of elongation at that point. It may be the same with TEA, and the elongation may have its maximum value at a concentration of 40 phr TEA. However, TEA-plasticized plastics had the highest elongation at 30 phr, which may be attributed to the excess of total plasticizers as much as 42.66% with addition of 40 phr TEA. For ST series, there was a sharp increase of elongation and a rapid decrease of tensile strength and Young's modulus of materials when the content of TEA increases from 20 to 30 phr. This dramatic change of mechanical properties could be attributed to the higher increment of total plasticizers (6.31%) when the content of TEA

increased from 20 to 30 phr compared with 4.59 ~ 5.24% when its content increased from 30 to 40 phr or from 40 to 50 phr. Overall, the mechanical properties of TEA plasticized protein plastics were better than that of DEA plasticized plastics. The conclusion from tensile tests was in good agreement with that from structure, optical properties, and TG tests. In addition, ST30 had nearly the same tensile strength with the control SG30 (5.03 MPa), however, a much higher elongation than that of SG30 (87.21%) at RH = 75%.

CONCLUSIONS

TEA exhibited the better plasticizing effect on soy protein plastics, compared with DEA and glycerol. TEA plasticized soy protein plastics possessed a better optical properties, lower WU, and higher mechanical properties than DEA and glycerol plasticized plastics. The glass transition temperature of the material with TEA was also higher than that plasticized with the other two. Moreover, the soy protein plastics with TEA had better thermal stability than those with DEA and glycerol, as a result of the strong interaction between TEA and protein molecules, leading to the good compatibility. The soy protein materials will be promising for the application in the fields of package and container, substituting for the nongreen polymers.

References

- Zhang, J.; Jiang, L.; Zhu, L.; Jane, J.-I.; Mungara, P. *Biomacromolecules* 2006, 7, 1551.

2. Micard, V.; Belamri, R.; Morel, M.-H.; Guilbert, S. *J Agric Food Chem* 2000, 48, 2948.
3. Chen, P.; Zhang, L. *Biomacromolecules* 2006, 7, 1700.
4. Chen, P.; Zhang, L.; Cao, F. *Macromol Biosci* 2005, 5, 872.
5. Lu, Y.; Larock, R. C.; *Biomacromolecules* 2007, 8, 3108.
6. Hishikawa, Y.; Togawa, E.; Kataoka, Y.; Kondo, T. *Polymer* 1999, 40, 7117.
7. Sue, H. J.; Wang, S.; Jane, J. L. *Polymer* 1997, 38, 5035.
8. Amass, W.; Amass, A.; Tighe, B. *Polym Int* 1998, 47, 89.
9. Sun, X.; Kim, H. R.; Mo, X. J. *J Am Oil Chem Soc* 1999, 76, 117.
10. Zhong, Z.; Sun, S. X. *Polymer* 2001, 42, 6961.
11. Lodha, P.; Neteravali, A. N. *J Mater Sci* 2002, 37, 3657.
12. Feng, L.; Wang, Y. Q.; Sun, X. S. *J Polym Eng* 1999, 19, 383.
13. Lodha, P.; Neteravali, A. N. *Ind Crops Prod* 2005, 21, 49.
14. Liu, D.; Zhang, L. *Macromol Mater Eng* 2006, 291, 820.
15. Liu, D.; Tian, H.; Zhang, L. *J Appl Polym Sci* 2007, 106, 130.
16. Irissin-Mangata, J.; Bauduin, G.; Boutevin, B.; Gontard, N. *Eur Polym Mater* 2001, 37, 1533.
17. Wu, Q.; Zhang, L. *J Appl Polym Sci* 2001, 82, 3373.
18. Anglès, M. N.; Dufresne, A. *Macromolecules* 2000, 33, 8344.
19. Gontard, N.; Guilbert, S.; Cuq, B. *J Food Sci* 1992, 57, 190.
20. MacDonald, G. M.; Barry, B. A. *Biochemistry* 1992, 31, 9848.
21. Wu, Q.; Zhang, L. *Ind Eng Chem Res* 2001, 40, 558.
22. Fekete, E.; Foldes, E.; Pukanszky, M. *Eur Polym Mater* 2005, 41, 727.
23. Chen, Y.; Zhang, L. *Ind Eng Chem Res* 2003, 42, 6786.
24. Chen, P.; Zhang, L. *Macromol Biosci* 2005, 5, 237.