

Mechanical Properties and Biodegradability of Crosslinked Soy Protein Isolate/Waterborne Polyurethane Composites

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ABSTRACT: With anionic waterborne polyurethane (WPU) as a plasticizer and ethylene glycol diglycidyl ether (EGDE) as a crosslinker, we successfully prepared crosslinked soy protein isolate (SPI) plastics. Anionic WPU was mixed with SPI and EGDE in an aqueous dispersion at room temperature. The mixed aqueous dispersion was cast and cured, and the obtained material was pickled and hot-pressed to produce the crosslinked SPI/WPU sheets. The resulting sheets containing about 60 wt % SPI were characterized with infrared spectroscopy, scanning electron microscopy, atomic force microscopy, dynamic mechanical analysis, and tensile testing, and biodegradation testing of

the sheets was performed in a mineral salt medium containing microorganisms. The results revealed that the crosslinked SPI/WPU plastics with EGDE concentrations of 2–4 wt % possessed high miscibility, good mechanical properties, and water resistivity. In addition, the crosslinked sheets could be biodegraded, and the half-life of the biodegradation for a sheet crosslinked with 3 wt % EGDE was calculated to be less than 1 month. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 465–473, 2005

Key words: biodegradable; crosslinking; miscibility; polyurethanes; proteins

INTRODUCTION

The significance of ecomaterials based on renewable natural resources and the limited nature of petrochemical resources have necessitated the development of polymers from agricultural processing products such as soy proteins from oil processing.¹ Soy proteins are abundant and relatively low cost and have been studied as polymers from a materials science perspective.² Recently, soy protein isolate (SPI) has been considered an alternative to petroleum polymers for adhesives, plastics, and various binders.³ The Technology Road Map for Plant/Crop-Based Renewable Resources 2020, sponsored by the U.S. Department of Energy, has targeted the achievement of 10% of basic chemical building blocks arising from plant-derived renewable source by 2020, with development concepts in place by then to achieve a further increase to 50% by 2050.⁴ However, the brittleness and water sensitivity of protein plastics limit their further applications. An improvement in the toughness and water resistivity of protein plastics is essential for their successful applications. Many efforts have been made to enhance the toughness of soy protein plastics through the addition

of plasticizers, such as water,⁵ glycerin,^{6,7} and ethylene glycol,⁸ but they became more water sensitive and were easily replaced by water when wet. Therefore, increasing the mechanical and waterproof properties of the soybean protein plastics and keeping their biodegradability present a very interesting problem.

Waterborne polyurethane (WPU) is regarded as a nontoxic, nonflammable,⁹ and biodegradable material.¹⁰ Its abundant amide groups ($-\text{CONH}-$)¹¹ give it excellent miscibility with SPI and immobility in the blend. Our recent work has proved that WPU as a plasticizer greatly enhances the toughness of SPI composites. The objective of this research was to improve further the strength of SPI/WPU plastics through the addition of ethylene glycol diglycidyl ether (EGDE) as the crosslinker and to clarify the biodegradability, which was evaluated with biodegradation testing in a medium containing *Aspergillus niger*. The morphology, structure, miscibility, mechanical properties, and water resistivity of the crosslinked SPI/WPU plastics were studied with infrared spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), dynamic mechanical analysis (DMA), and tensile testing.

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EXPERIMENTAL

Materials

All the chemicals were commercially available in China. EGDE (epoxide number = 0.8 mol/100 g) was

purchased from Yueyang Epoxy Resin Co. (Hunan, China). SPI (dry basis protein content = 91%) was purchased from Dupont-Yunmeng Protein Technology Co. (Hubei, China) and vacuum-dried at 60°C for 4 h to make the moisture content of SPI lower than 2 wt %. Poly(oxypropylene glycol) (PPG; number-average molecular weight = 1000) as a soft segment in the composites was vacuum-dried at 120°C for 1 h. Dimethylolpropionic acid (DMPA) was chemically pure and was purchased from Anqin Chemical Co. (Anhui, China). DMPA was used as a chain extender and anionic center and was dried at 100°C for 1 h. Triethylamine (TEA) and acetone (an analytical reagent) were purchased from Shanghai Reagent Co. (Shanghai, China) and were dried with molecular sieves (4 Å) for more than a week before use. The other reagents were used without further purification.

Preparation of the polyurethane aqueous dispersions

PPG (66 g, 0.066 mol) and toluene diisocyanate (20 g, 0.115 mol) were added to a four-necked flask equipped with a thermometer, stirrer, dropping funnel, and condenser. The resulting mixture was stirred at 80°C for 60 min, and then DMPA (2.68 g, 0.02 mol) was added. The reaction was performed at 85°C for 2–3 h. After the reaction mixture was cooled to 40–50°C, 30 g of acetone was added to reduce the viscosity of the prepolymer, TEA (2.1 g, 0.02 mol) was added to neutralize the carboxylic groups of DMPA, and then deionized water (710 g) was added to emulsify. Ethylenediamine (0.12 g, 0.02 mol) as a chain extender was dropped into the aqueous dispersion, and the dispersion was stirred for 3 h to obtain a stable WPU dispersion (concentration = 10 wt %).

Preparation of the specimens

SPI, water, and WPU (concentration = 10 wt %) were thoroughly mixed in a 6:54:40 ratio by weight and stirred for 0.5 h. Then, a desired amount of EGDE was added. The resulting mixture was cast onto a Teflon mold and placed in an oven at 50°C for 24 h to form dry sheets containing about 60 wt % SPI. The sheets were immersed in a 0.5M acetic acid aqueous solution for 24 h and then were taken and placed in air at 25°C for 24 h. The resulting materials were compression-molded under 20 MPa at 115–120°C for 10 min to give sheets with a thickness of 0.3 mm. Through changes in the EGDE content from 0 to 6 wt %, a series of blend sheets were prepared, and they were coded E0, E1, E2, E3, E4, E5, and E6, corresponding to EGDE concentrations of 0, 1, 2, 3, 4, 5, and 6 wt %, respectively. The sheets prepared from pure WPU and SPI were coded WPU and SPI, respectively.

Apparatus and characterization

Surface Fourier transform infrared (FTIR) spectra of the samples were recorded on a spectrometer (170SX, Nicolet, Madison, WI) at room temperature. The cross-section morphology of the sheets was observed with a scanning electron microscope (S-570, Hitachi, Tokyo, Japan) with 20 kV as the accelerating voltage and were recorded on 35-mm film. The sheets were frozen in liquid nitrogen, fractured immediately, and then vacuum-dried. The cross sections of the sheets were coated with gold before SEM observation. The surface morphology of the sheets was observed with an atomic force microscope (NanoScope III system, Digital Instruments, Santa Barbara, CA) in air and at room temperature in the tapping mode with silicon tips (Digital Instruments). The samples were attached to the sample holder with double-sided tape. The resonant oscillating frequencies were around 310 kHz, and the scanning rates were 1.02 Hz. DMA was carried out on a dynamic mechanical thermal analyzer (DMTA-V, Rheometric Scientific Co., Piscataway, NJ) at 1 Hz and a heating rate of 5°C/min from –80 to 150°C. Sheets with a typical size of 10 mm × 10 mm were used. Each sheet was repeated three times, and the results were averaged.

The stress–strain (σ – ϵ) values of the sheets were measured on a universal tester (CMT-6503, Shenzhen SANS Test Machine Co., Ltd., Guangdong, China) according to ISO6239-1986 (E) at a tensile speed of 50 mm/min. However, because of the excessive elongation of the WPU sheets, we had to cut it before breaking it during the testing. To obtain the σ – ϵ curves of the sheets in the wet state, we immersed the sheets in water at 25°C for 4 h, and then the σ – ϵ curves of the sheets in the wet state were measured with the same procedure used for the dry state. Each sheet was repeated five times, and the results were averaged. The water absorption was measured according to ASTM Standard D 570-81 (ASTM D 570-81, 1993). The sheets were preconditioned by drying in an air oven at 50°C for 24 h. After being cooled in a desiccator for a few minutes, the dry sheets were weighed (W_1). Then, the sheets were submerged in distilled water at $25 \pm 2^\circ\text{C}$ for 24 h. After their removal from water, the extra water on the surface of the sheets was removed with a paper towel, and the sheets were weighed again (W_2). The absorbed water content (W_{water}) was calculated as follows:

$$W_{\text{water}} = [(W_2 - W_1)/W_1] \times 100\% \quad (1)$$

The wet sheets were dried in an oven at 60°C for 24 h and weighed again (W_3); the weight loss of the sheets (W_{loss}) was calculated as follows:

$$W_{\text{loss}} = [(W_1 - W_3)/W_1] \times 100\% \quad (2)$$

Each sheet was repeated two times, and the results were averaged.

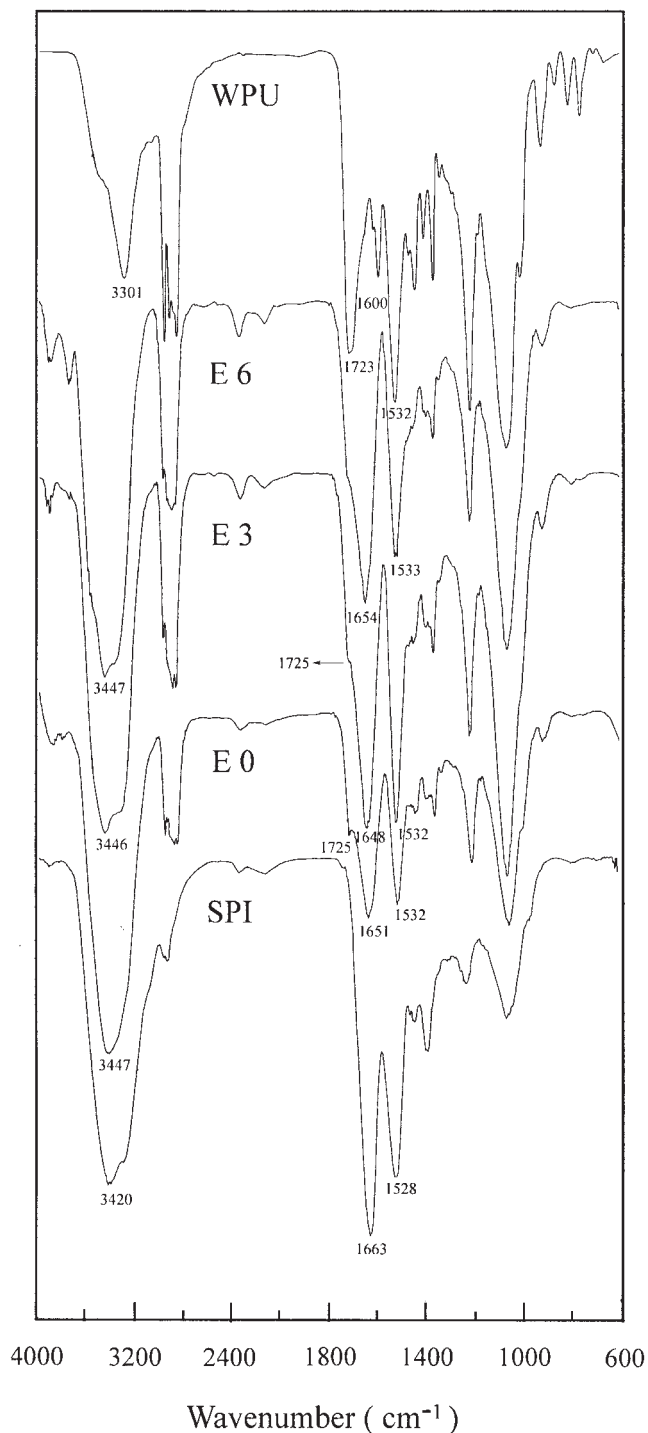


Figure 1 FTIR spectra of the WPU, E0, E3, E6, and SPI sheets.

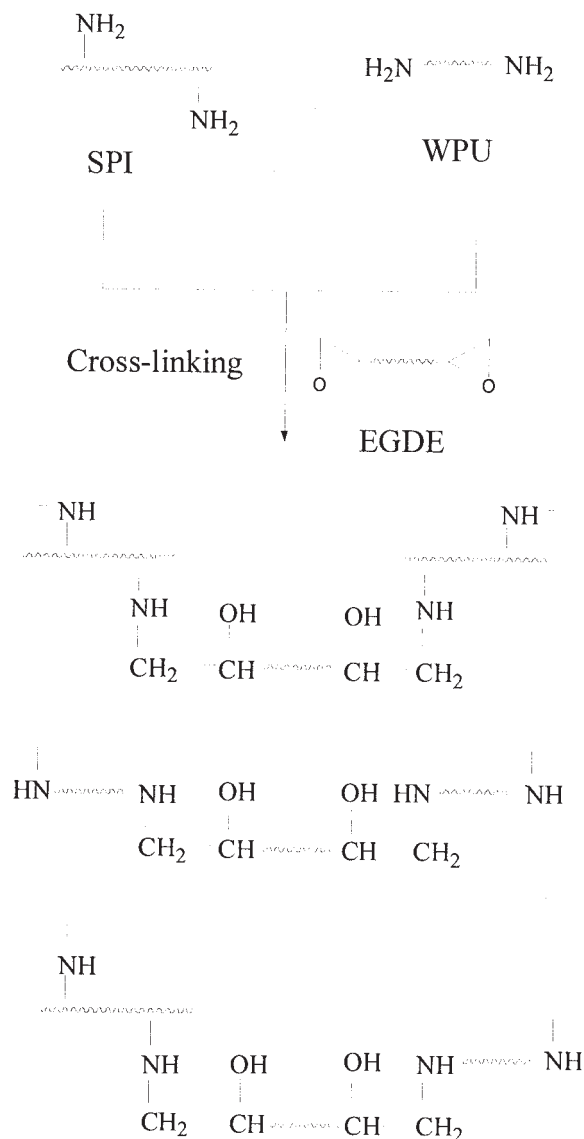
Biodegradation test

A. niger were supplied by the China Center for Type Culture Collection at Wuhan University (Wuhan, China). A mineral salt medium was used that contained 0.7 g/L KH_2PO_4 , 1.0 g/L NH_4NO_3 , 0.002 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.002 g/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.005 g/L NaCl, with the pH adjusted to 6.5 by the addition of a

0.01 mol/L NaOH aqueous solution. The medium and culture dish were sterilized via autoclaving at 120°C for 20 min. Inoculation operations were carried out on an asepsis table. The mineral salt medium (30 mL) was injected into each culture dish (diameter = 18 cm). The dried sheets ($2 \times 2 \times 0.3 \text{ cm}^3$) were weighed (W_a) and immersed in the mineral salt medium (sheet/ culture dish), and then the culture dishes were moved into the desiccators, which were placed in an incubator; the temperature was kept at $30 \pm 1^\circ\text{C}$. Every 5 days, a sheet was taken from desiccators and water-washed slightly, dried at 60°C for 24 h, and weighed (W_b). The extent of biodegradation (R) was given by

$$R = [(W_a - W_b) / W_a] \times 100\% \quad (3)$$

Each sheet was repeated two times, and the results were averaged.



Scheme 1 Grafting and crosslinking of EGDE on SPI and WPU.

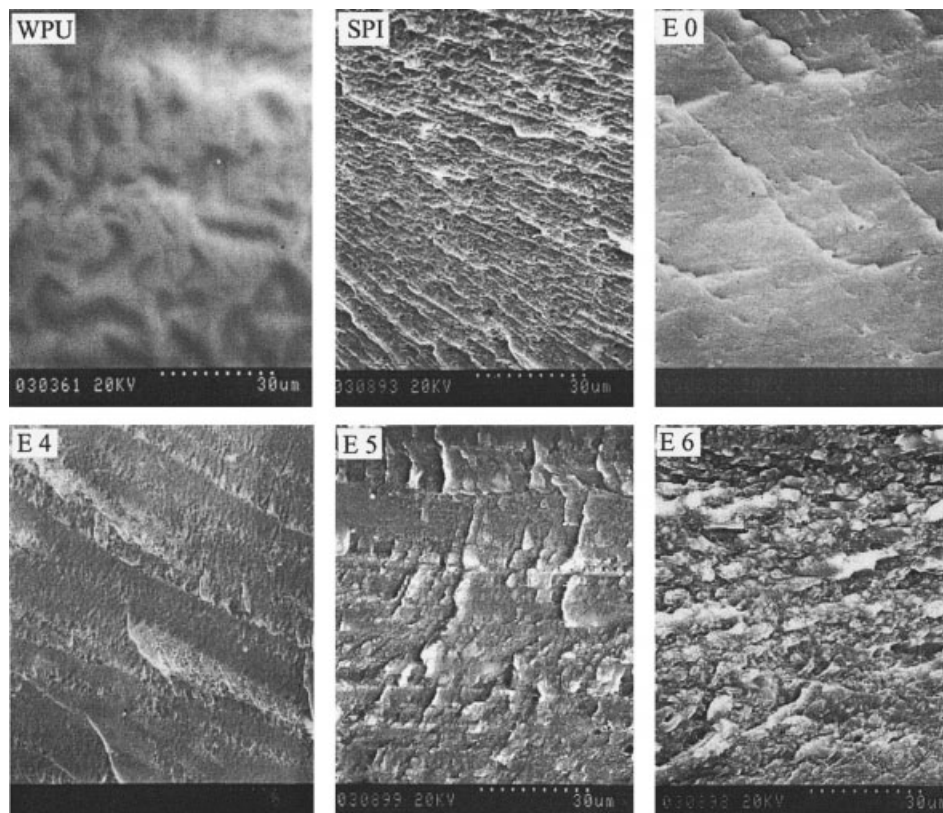


Figure 2 SEM images of the cross sections of the WPU, SPI, E0, E4, E5, and E6 sheets.

For the observation of the surfaces of the degraded sheets, the sheets, biodegraded for 10 days, were washed slightly with water and vacuum-dried. The surfaces were coated with gold and observed with SEM.

RESULTS AND DISCUSSION

Structure and miscibility

FTIR spectra of the WPU, E0, E3, E6, and SPI sheets are shown in Figure 1. The WPU sheet exhibited the char-

acteristic absorption peaks at 3301 (N—H stretch), 1723 (C=O stretch), and 1532 cm^{-1} (N—H bending).^{12–14} The absorption peaks of SPI were located at 1663 (hydrogen-bonded C=O stretch) and 1528 cm^{-1} (N—H bending).¹⁵ The absorption peaks for SPI at 1651 cm^{-1} in the WPU blended sheets of E0 (shifting to lower wave numbers in comparison with SPI at 1663 cm^{-1}) indicated that there was environmental change for the SPI chains, that is, stronger hydrogen bonding between SPI and WPU. With an increase in EGDE, the absorption peak frequency remained. As

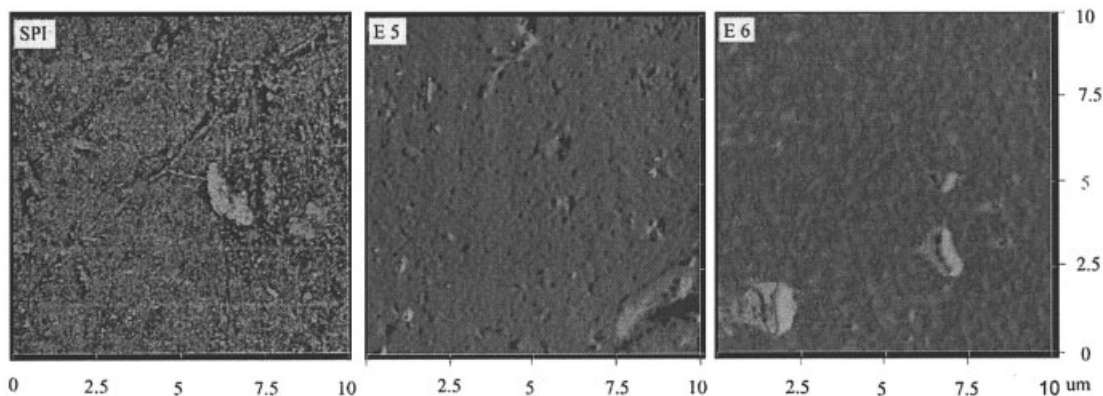


Figure 3 AFM phase images of the surfaces of the SPI, E5, and E6 sheets.

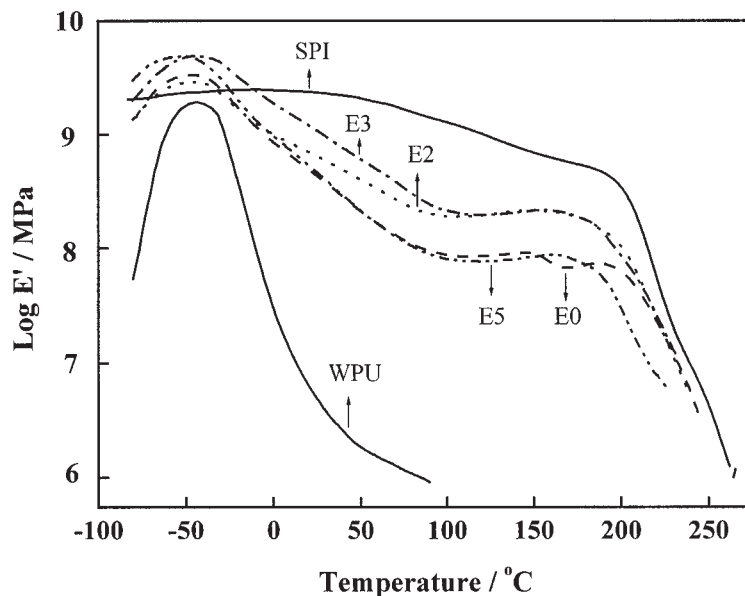


Figure 4 Dependence of E' on the temperature for the E0, E1, E2, E3, and E5 sheets.

for WPU, the intensity of the peak at 1725 cm^{-1} of the E0 sheet decreased with increasing EGDE content. This was due to the reaction between the epoxy groups of EGDE and the amino groups of WPU because the amino groups were much more nucleophilic in the carbamates ($-\text{NH}-\text{CO}-\text{O}-$) than those in the amide groups ($-\text{CO}-\text{NH}-$). This suggested also the formation of a network of EGDE-crosslinked SPI/WPU composites, as shown in Scheme 1.

The SEM photographs of the cross sections for the sheets are shown in Figure 2. The WPU and SPI sheets showed homogeneous morphology. The

blend sheets E0 and E4 showed homogeneous morphology, but slight phase separation appeared for E5, and it became more severe for E6. The AFM phase images of the sheets are shown in Figure 3. SPI showed no smooth surface. The sheets E5 and E6 showed smooth surface. This indicated certain miscibility between SPI and WPU in the blend materials, and this was attributed to the strong intermolecular hydrogen bonding between WPU and SPI macromolecules by amide groups ($-\text{CONH}-$) in amide and carbamate. As observed with SEM, phase separation in E5 and E6 was exhibited, and this

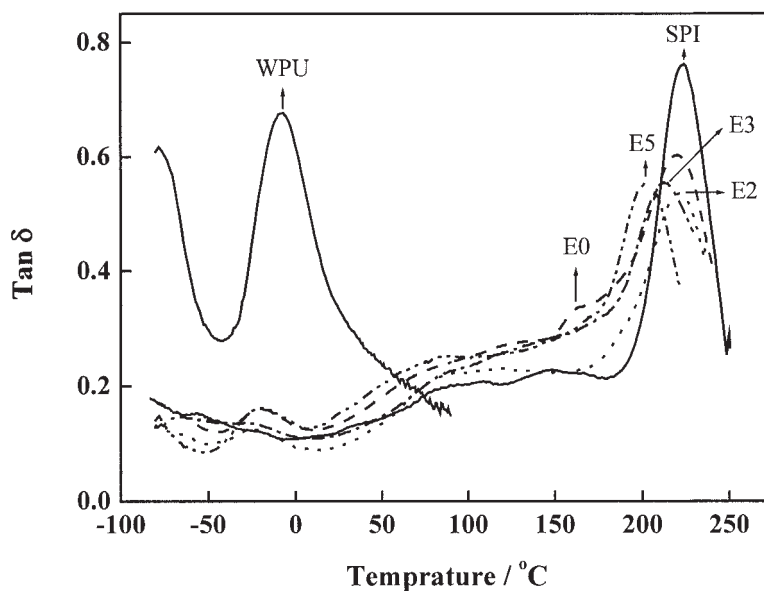


Figure 5 Dependence of $\tan \delta$ on the temperature for the E0, E1, E2, E3, and E5 sheets.

TABLE I
Data of the E0, E1, E2, E3, E4, E5, and
E6 Sheets from DMA

Sheet	T_g (°C)	T_{d2} (°C)
WPU	-8.34	—
E0	-20.1	220.3
E1	-23.7	221.0
E2	-25.2	221.3
E3	-26.7	214.6
E4	-24.2	213.4
E5	-21.8	202.6
E6	-19.5	202.3
SPI	—	222.4

suggested that an EGDE concentration below 5 wt % was appropriate in terms of SPI/WPU miscibility.

Thermal properties

The dependence of the storage modulus (E') on the temperature for the sheets is shown in Figure 4. The modulus of the E0, E2, E3, E5, and SPI sheets at 25°C was significantly higher than that of WPU (SPI > E3 > E2 > E0–E5). The results indicated that the induction of WPU reduced the stiffness of SPI. The dependence of the mechanical loss factor ($\tan \delta$) on the temperature for the sheets is shown in Figure 5, and the corresponding data are summarized in Table I. The $\tan \delta$ value is related to the glass-transition temperature (T_g)¹⁶ and other transitions. The $\tan \delta$ peaks of WPU at -8.3°C were assigned to T_g of the soft segment. The $\tan \delta$ peaks of SPI at 222.5°C were assigned to the decomposition transition (T_{d2}), respectively. T_g of the blend sheets shifted to a lower tem-

perature. This was a result of the effects of the —CONH— groups on the molecules of SPI and WPU; that is, the stronger interaction between SPI and WPU weakened the interaction between the soft and hard segments in WPU. For EGDE-crosslinked sheets, with the addition of EGDE, which reacted with WPU, leading to a reduction of the interaction between the hard and soft domains, the T_g values of E1–E5 decreased. However, a continual increase in EGDE led to phase-separation because the solubility of EGDE in water was very low at room temperature (solubility < 0.5 wt %) and finally overturned the effect, resulting in an elevation of T_g of E6.¹⁷ The $\tan \delta$ peak at about 170°C of the E0 blend sheet was assigned to the melting temperature (T_m) of WPU. With an increase in the EGDE content, T_m for blend sheets E1, E2, E3, E4, E5, and E6 did not appear, and this further proved that the crosslinking reaction occurred in the SPI/WPU sheets because the crosslinked WPU had no T_m . $T_{d,2}$ of E0–E2 was close to that of soy protein. However, with an increase in the EGDE content, the decomposition temperature of blends E3–E6 slightly decreased because of the relatively low thermal stability.

Mechanical properties and water resistivity

The σ - ϵ curves of the E1, E2, E3, E4, E5, and E6 sheets are shown in Figure 6. The tensile strength (σ_b) values increased and elongation at break (ϵ_b) decreased with an increase in the EGDE content when the EGDE content was less than 3 wt %. However, when the EGDE content was greater than 3 wt % and less than 5 wt %, the σ_b values decreased and ϵ_b increased. When the EGDE content was greater than 5 wt %, both

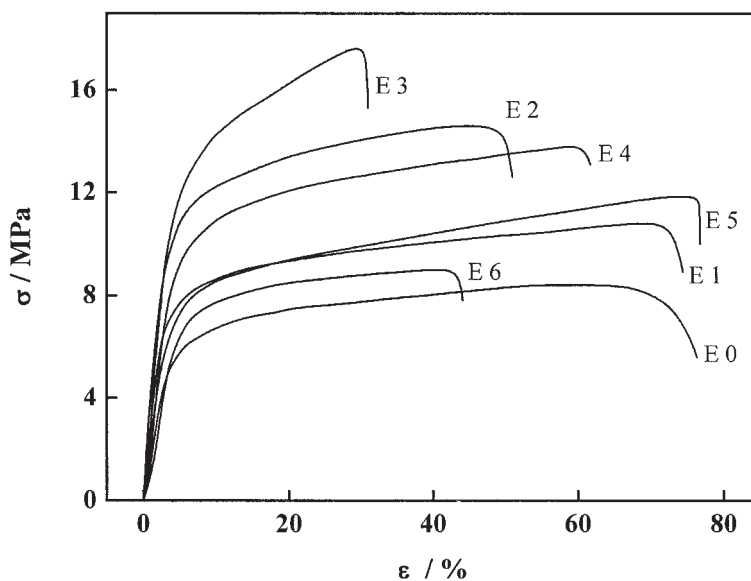


Figure 6 σ - ϵ curves for the E0, E1, E2, E3, E5, and E6 sheets in the dry state.

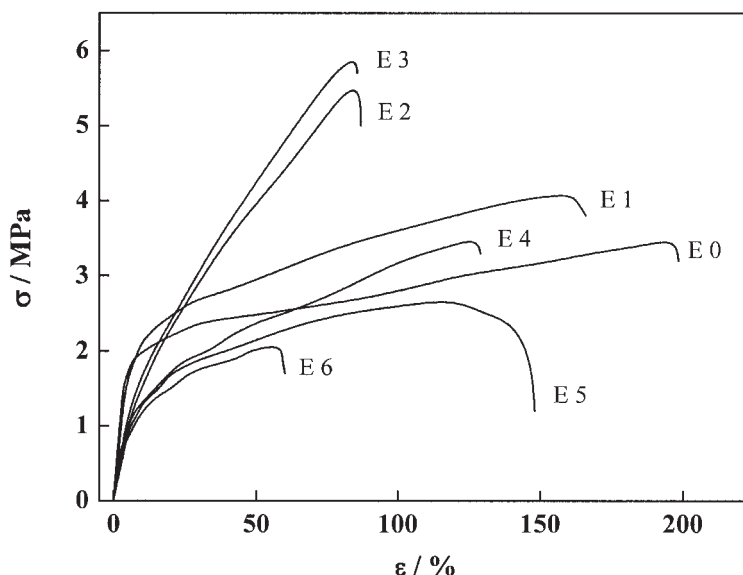


Figure 7 σ - ε curves for the E0, E1, E2, E3, E5, and E6 sheets in the wet state.

σ_b and ε_b decreased. The area under the strain-stress curves could be used to estimate the toughness of specimens. The relatively large area of sheets E1-E5 indicated the character of toughened plastics. When the EGDE content was 3 wt %, the values of σ_b and ε_b of the E3 sheet reached 18 MPa and 25%, respectively.

In addition, the σ - ε curves of the blend sheets in the wet state with different EGDE contents are shown in Figure 7. Crosslinked materials E1-E4 exhibited higher tensile strength than uncrosslinked materials. However, all the crosslinked SPI/WPU plastics possessed lower elongation at break than that without a crosslinker (E0). The mechanical strength of E5 and E6 (especially E6) was lower than that of E0, E2, E3, and E4, and this implied that a concentration of the crosslinker (EGDE) greater than 5 wt % was not advantageous for the miscibility of the composites. The excessive crosslinker resulted in phase separation and a reduction of the mechanical properties. Sheet E3, with about 3 wt % EGDE, exhibited good mechanical properties and miscibility.

Table II shows the water absorption of the sheets in distilled water at $25 \pm 2^\circ\text{C}$ for 24 h and the weight loss in distilled water at $25 \pm 2^\circ\text{C}$ for 24 h. The difference in the water absorption and weight loss was not obvious among the E0, E1, E2, E3, and E4 sheets. How-

ever, the water absorption and weight loss increased severely for the E5 and E6 sheets because of the phase separation. The results agreed with the results of the infrared, SEM, AFM, and mechanical testing.

Biodegradation tests

The SEM photographs of the surfaces of the sheets before and after biodegradation in a medium containing *A. niger* at 30°C for 10 days are shown in Figure 8. The original sheets (SPI, E0, and E3) had smooth surfaces. However, the biodegraded sheets (SPI-b, E0-b, and E3-b) exhibited porous structures in the surfaces corroded by the microorganism. The extent of biodegradation was in the order of SPI > E0 > E3. Plots of the degree of degradation against the degradation time for the sheets are shown in Figure 9. Under the same conditions, the SPI sheet was biodegraded completely within 20 days, whereas the *R* values for the E0 and E3 sheets were 43.7 and 38.8 wt %, respectively. Moreover, the half-lives of the SPI, E0, and E3 sheets were 15, 23, and 28 days, respectively. The results indicated that the crosslinked SPI/WPU materials could be biodegraded, and the half-life was no longer than a month.

TABLE II
Water Absorption and Weight-Loss Rate of the WPU, E0, E1, E2, E3, E4, E5, E6, and SPI Sheets

	Sheet								
	WPU	E0	E1	E2	E3	E4	E5	E6	SPI
W_{water} (%)	14.6 ± 0.5	26.5 ± 0.5	26.6 ± 0.5	25.9 ± 0.5	26.7 ± 0.5	27.6 ± 0.5	32.8 ± 0.5	36.1 ± 0.5	38.7 ± 0.5
W_{loss} (%)	0.1 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	1.2 ± 0.1	3.7 ± 0.5

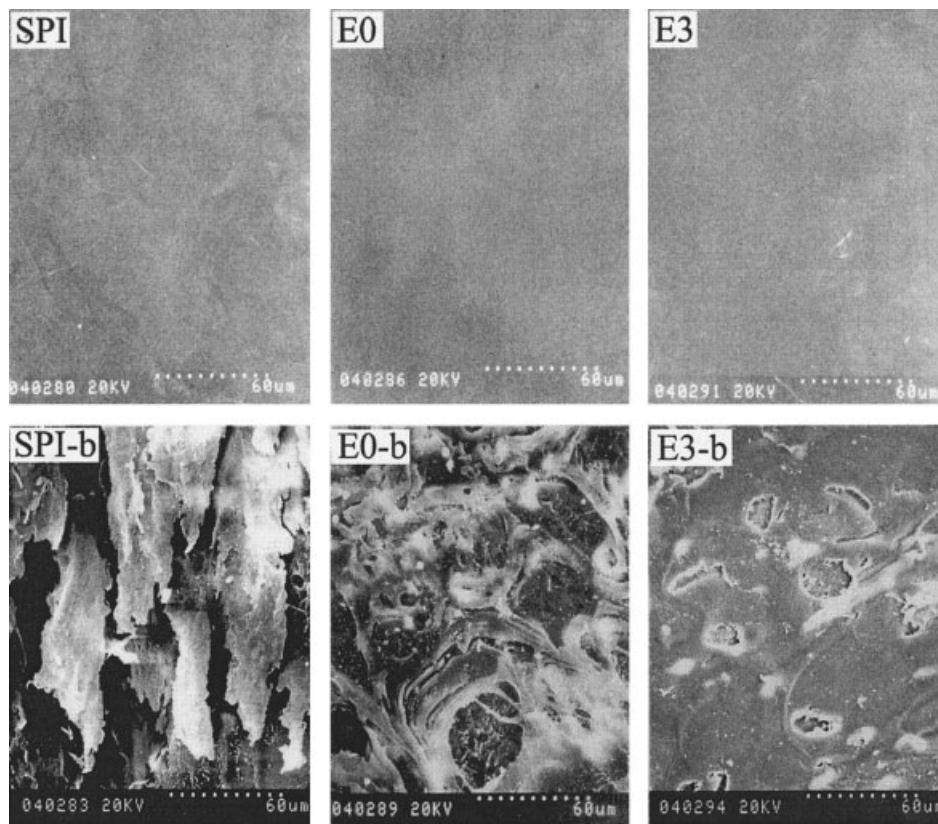


Figure 8 SEM images of the surfaces of the sheets before (SPI, E0, and E3) and after (SPI-b, E0-b, and E3-b) biodegradation in a medium containing *A. niger* at 30°C for 10 days.

CONCLUSIONS

Crosslinked SPI/WPU plastics were successfully prepared from anionic WPU, SPI, and a crosslinker

(EGDE). When the EGDE content was about 3 wt %, the EGDE-crosslinked SPI/WPU sheets presented high miscibility, good mechanical strength (dry state: $\sigma_b = 18$ MPa and $\varepsilon_b = 30\%$; wet state: $\sigma_b = 6$ MPa and

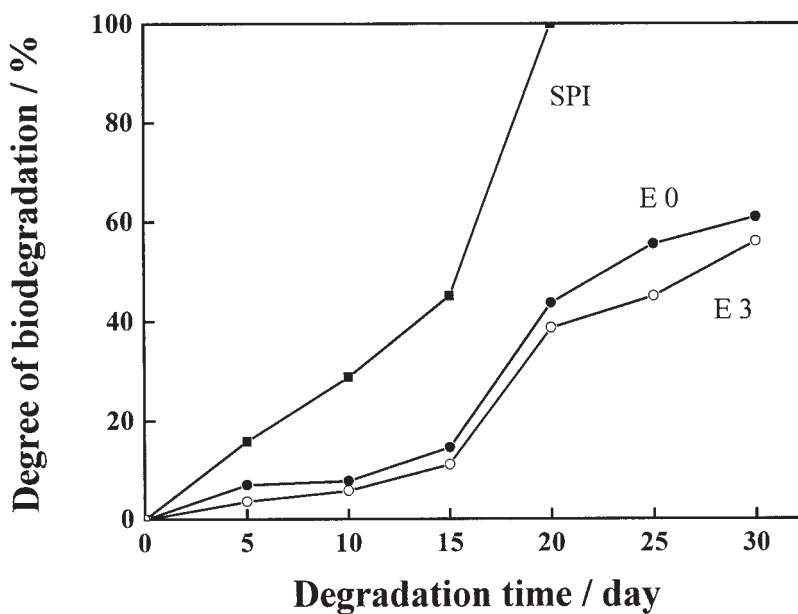


Figure 9 Plots of the degree of biodegradation against the degradation time of SPI, E0, and E3 sheets in the medium containing *A. niger* at 30°C.

$\varepsilon_b = 90\%$), thermal stability, and water resistance ($W_{\text{water}} = 26.7 \text{ wt } \%$ and $W_{\text{loss}} = 0.6 \text{ wt } \%$). Through crosslinking with EGDE, the mechanical properties of the SPI/WPU blends were improved as a result of the interactions of peptides in SPI and urethane bonds in WPU. Moreover, the crosslinked SPI/WPU plastics were biodegradable by *A. niger*, with a half-life of less than 1 month for E3.

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