

Properties of Crosslinked Casein/Waterborne Polyurethane Composites

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Received 21 October 2002; accepted 2 May 2003

ABSTRACT: Waterborne polyurethane (WPU) and casein (1 : 1 by weight) were blended at 90°C for 30 min, and then were crosslinked by adding 1–10 wt % ethanedial to prepare a series of sheets. Their structure and properties were characterized by using infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, dynamic mechanical analysis, and tensile testing. The results indicated that crosslinked blend sheets exhibited a certain degree of miscibility, and exhibited much higher tensile strength and water resistivity than did the WPU, casein, and the uncrosslinked blend from WPU and casein. When the ethanedial content was 2 wt %, the tensile

strength and elongation at break of crosslinked sheets achieved 19.5 MPa and 148% in the dry state, and 5.0 MPa and 175% in the wet state, respectively. A 2 wt % content of ethanedial plays an important role in the enhancement of mechanical properties, thermal stability, and water resistivity of the blends of WPU and casein as a result of intermolecular crosslinking. This work provided a new protein plastic with good water resistivity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 332–338, 2004

Key words: polyurethane; proteins; blends; crosslinking; miscibility

INTRODUCTION

Recently, environmentally friendly materials based on natural polymers have attracted much attention.¹ Casein, as a natural protein, has been used as the raw material for application in many fields, such as progesterone release from casein microspheres, which were fabricated by glutaraldehyde crosslinking of an aqueous alkaline solution of the protein dispersed in a hexane and dichloromethane nonaqueous dispersion medium with an aliphatic polyurethane as the stabilizer,² adhesion,³ and printing,⁴ for example. However, further applications are limited by the lack of water resistivity and the brittle characteristics of casein sheet. Blending natural polymers with other polymers is an interesting way to improve physical properties of the materials. Waterborne polyurethane (WPU) is regarded as a nontoxic, nonflammable, and universal material. Anionic waterborne polyurethane, the most common one, can be prepared from polyols containing carboxylic acid and sulfonic acid groups. However, steric hindrance of the polyol prevents the potential reaction of the acid group with the isocyanate during preparation. To achieve solubility, the acid groups can be neutralized using basic compounds (e.g., tertiary amines). Thus, the waterborne polyurethane will come to dominate with sustained

growth in the building and automotive electrodeposition coatings markets.⁵ It is worth noting that casein and WPU all contain –CONH– groups on their molecules, so that their blend should have good miscibility. However, the water resistivity of the blends is difficult to be enhanced because of existence of hydrophilic groups. A basic improvement of the water resistivity for the casein is essential for its wider application.

In our laboratory, the miscibility, structure, and properties of blend membranes from cellulose with other polymers such as casein and alginate have been investigated, and they have exhibited excellent mechanical properties and some functions.^{6–8} In this work, we attempted to synthesize WPU and then to blend WPU with casein in aqueous solution. To enhance water resistivity, the ethanedial was added in the blends to form crosslinking through reaction between –NH₂ groups of casein and WPU and –CHO groups of ethanedial. The effects of ethanedial content on miscibility, structure, mechanical properties, water resistivity, and thermal stability of the blends were investigated by infrared spectroscopy (IR), scanning electron micrography (SEM), tensile testing, dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

All the chemical reagents used here were obtained from commercial sources in China. 2,4-Toluene diiso-

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cyanate (TDI) was used as the hard-segments composite. Polyoxypropylene glycol (PPG; $M_w = 1000$) as the soft-segments composite was vacuum dried at 120°C for 1 h. Dimethylolpropionic acid (DMPA), as chain extender and anionic center, was dried at 100°C for 1 h. Triethylamine (TEA) and acetone were dried over 4-Å molecular sieves for more than a week before use. Ethanedial (40 wt % aqueous solution, supplied by Shanghai Chemical Reagent Plant) was diluted to be 10 wt % aqueous solution before use. The other reagents were used without further purification.

Preparation of waterborne polyurethane

Anionic WPU was synthesized as follows: PPG1000 (58 g, 0.058 mol) and TDI (20 g, 0.111 mol) were introduced by pouring into a four-neck flask equipped with a thermometer, stirrer, dropping funnel, and a condenser tube. The resulting mixture was stirred and heated to 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 until the –NCO content reached a desired value, which was determined by using a standard dibutylamine titration method.⁹ After cooling the reaction mixture to 40–50°C, 30 g acetone was added to reduce the viscosity of prepolymer, and the carboxylic groups of DMPA were neutralized with TEA (2.1 g, 0.02 mol). Finally, 710 g deionized water was added to emulsify, and then 10 wt % ethylenediamine aqueous solution (12 g, 0.02 mol) was added to extend the chain at room temperature. The excessive –NCO groups reacted with H₂O to produce –NH₂ groups and CO₂ slowly; thus the ending groups of some WPU molecules can be formed –NH₂ groups. Thus 10 wt % WPU was obtained.

Preparation of crosslinked WPU/casein sheets

Casein (10 g) was dispersed in 88 g deionized water with stirring at room temperature. TEA (2 g) was added and heated at 90°C for 30 min to prepare 10 wt % casein aqueous solution. The same quantity of WPU and casein solution were mixed and stirred at room temperature for 1 h, and then the desired amount of 10 wt % aqueous ethanedial was added. The resulting mixture was degassed and cast onto a Teflon mold. The casting solution was heated at 50°C for 10 h, then at 80°C for 2 h to obtain the transparent sheets with thickness of about 0.25 mm. By changing the weight ratio of ethanedial in solid content to be 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 wt %, a series of crosslinked casein/polyurethane sheets were prepared, and coded as UC50-0, UC50-1, UC50-2, UC50-3, UC50-4, UC50-5, UC50-6, UC50-7, UC50-8, UC50-9, and UC50-10, respectively. The sheets prepared from casein/TEA aquatic solution and pure WPU were coded as casein and WPU sheets, respectively.

Apparatus and characterization

The cross-section morphology of the sheets was observed using a scanning electron microscope (SEM; Hitachi S-570, Ibaraki, Japan). The samples were frozen in liquid nitrogen, fractured, and coated with gold before observation.

FTIR spectra of the samples were recorded in a spectrometer (Nicolet 170SX; Nicolet Analytical Instruments, Madison, WI) using KBr pellets at room temperature.

DMA was carried out with a dynamic mechanical thermal analyzer (DMTA-V; Rheometric Scientific Co., Amherst, MA) at 1 Hz and a heating rate of 5°C/min in the temperature range from –80 to 250°C under N₂ purge. The specimens with typical size of 10 × 10 mm (length × width) were used here.

The TGA curves of the samples were recorded on a TG 209 thermoanalyzer (Netzsch Co., Germany) under an air atmosphere from 30 to 530°C at a heating rate of 10°C/min. The starting decomposition temperature and weight loss values of the samples were evaluated by using the intersection point of tangents of TGA curves.

The tensile strength (σ_b) and elongation at break (ε_b) of the sheets were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., China) at a tensile speed of 50 mm/min according to ISO6239-1986 (E). An average value of five replicates for each sheet was taken. To obtain the σ_b (wet) of the sheets in the wet state, the sheets were soaked in water for 30 min at room temperature before testing. In addition, the absorbed water content (W_{H_2O}) in the sheets was measured according to ISO62-1980 (E), for a sheet immersed in water at 25°C for 3 h. The W_{H_2O} value was calculated as follows:

$$W_{H_2O} = [(W_2 - W_1)/W_2] \times 100 \quad (1)$$

where W_1 and W_2 are the weight of dry and swollen sheets, respectively. The wet sheets were dried in an oven at 80°C for 3 h and weighed; the following relation calculated the weight loss of sheets:

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

where W_1 and W_3 are the weight of original sheet and dried sheet after water immersion for 3 h, respectively.

RESULTS AND DISCUSSION

Structure and miscibility

FTIR spectra of the WPU, casein, and UC50 sheets are shown in Figure 1. The WPU sheet exhibited the characteristic absorption peaks at about 3300 cm⁻¹ (N—H stretch), 1723 cm⁻¹ (C=O stretch), and 1532 cm⁻¹

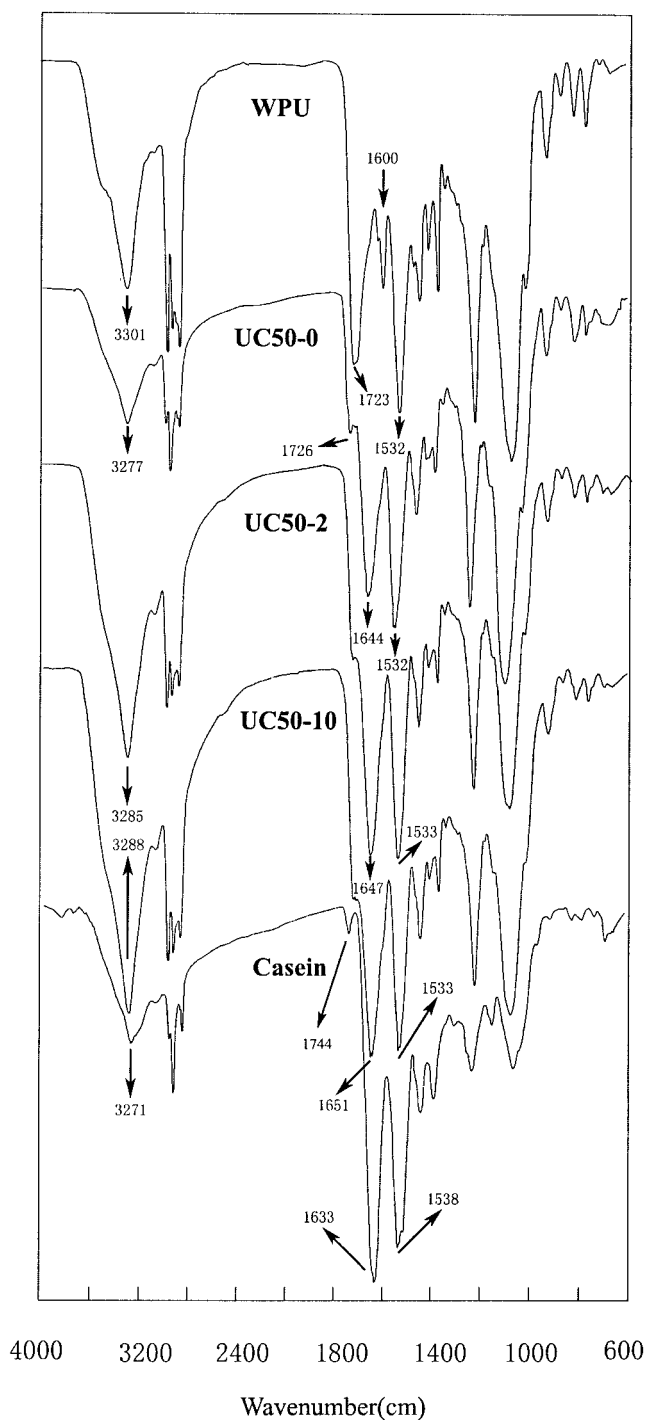


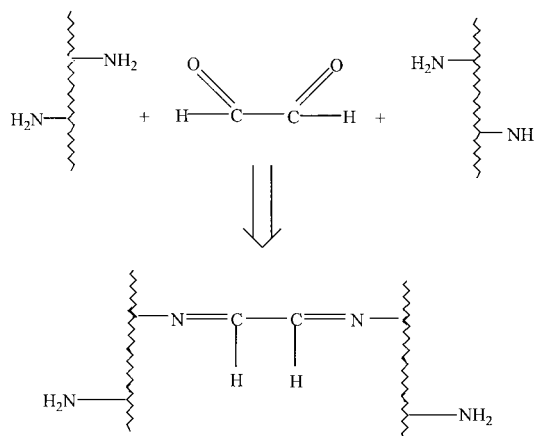
Figure 1 FTIR spectra of WPU, UC50-0, UC50-2, UC50-10, and casein sheets.

(N—H bending and C—N stretch).¹⁰⁻¹² The absorption peaks of casein were located at 1633 and 1730 cm^{-1} (hydrogen-bonded $\text{C}=\text{O}$ stretch in urea) and 1538 cm^{-1} (N—H bending and C—N stretch).^{13,14} However, the absorption peaks for casein appeared at 1644, 1647, and 1651 cm^{-1} in the sheets of UC50-0, UC50-2, and UC50-10, respectively, and moved to higher wavenumbers with an increase of ethanedial,

which may be attributed to the stretch vibration of $\text{C}=\text{N}$ groups resulting from the reaction of NH_2 in casein and WPU with $\text{CH}=\text{O}$ of ethanedial.¹⁵⁻¹⁷ This suggests the occurrence of a network in the UC50-2 and UC50-10 sheets as shown in Scheme 1.

The SEM photographs of the sheets are shown in Figure 2. The WPU and casein sheets showed homogeneous morphology, but the cross section of the pure casein sheet showed a few microporous structures. The cross section of UC50-0 sheets exhibited an overall homogeneous structure, indicating the occurrence of a certain degree of miscibility between the two components. When 2 wt % ethanedial was added, the UC50-2 sheets showed microphase separation. With increasing of ethanedial content, the UC50-5 sheets containing 5% ethanedial clearly showed microphase separation.

The dependency of storage modulus (E') on temperature for the sheets is shown in Figure 3. In views of E' curves of the sheets, stiffness at 30°C was in the order casein > UC50-10 > UC50-2 > UC50-0 > WPU sheets. The E' values of UC50-2 and UC50-10 sheets were greater than that of the UC50-0 sheets, attributed to the crosslinking. Two major relaxations corresponding to casein and WPU were clearly observed in the E' curves for the UC50-0, UC50-2, UC50-5, and UC50-10 sheets, indicating a certain degree of phase separation. The dependency of mechanical loss factor ($\tan \delta$) on temperature for the sheets is shown in Figure 4, and the corresponding data are summarized in Table I. The $\tan \delta$ was related with the glass transition (T_g) and the damping capacity of PU soft domains.¹⁸ The $\tan \delta$ of the WPU sheet appeared at about 25°C, which was assigned to glass transition coded as T_{g1} . The T_g of one component of casein was located at 100°C coded as T_{g2} , and that of another component of casein was located at 187°C coded as T_{g3} here. Interestingly, when the ethanedial was added, the $\tan \delta$ for the WPU phase



Scheme 1 Crosslinking reaction for NH_2 on casein and WPU with $\text{CH}=\text{O}$ on ethanedial.

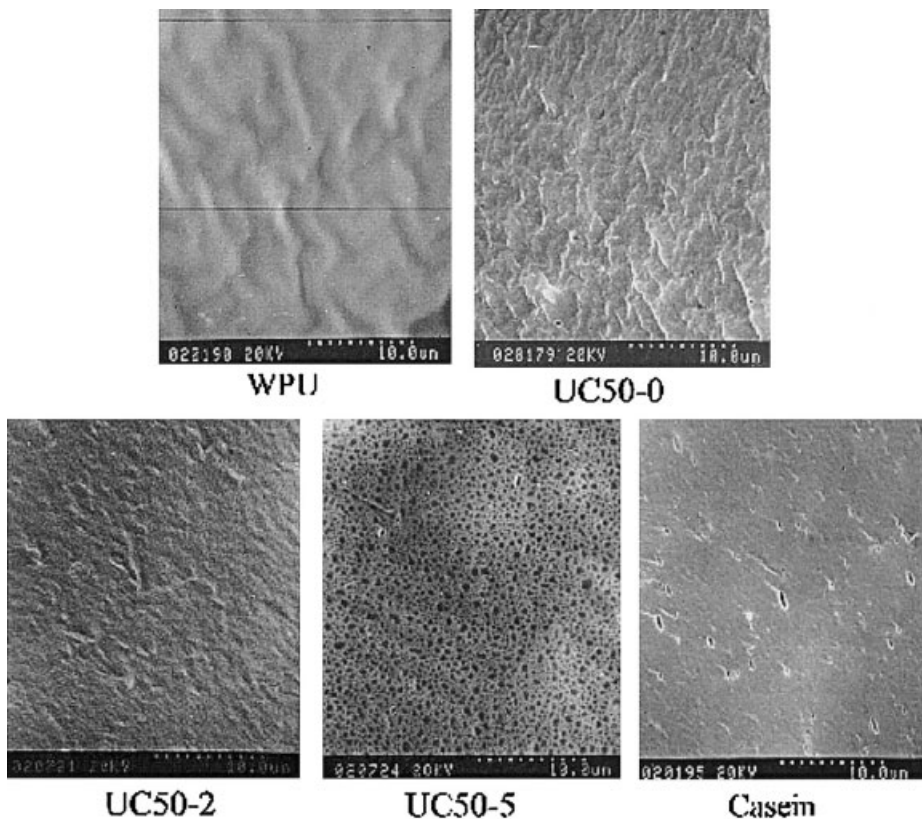


Figure 2 SEM photographs of cross section of WPU, UC20-0, UC50-0, UC50-2, UC50-5, and casein sheets.

in the UC50-2, UC50-5, and UC50-10 sheets shifted to a relatively low temperature, compared with that of UC50-0 and pure WPU sheets. The reduced value of T_{g1} of the UC50-2, UC50-5, and UC50-10 sheets indicated good binding between WPU and casein, resulting in a microphase separation between the soft and hard segments in the WPU domain, similar to the

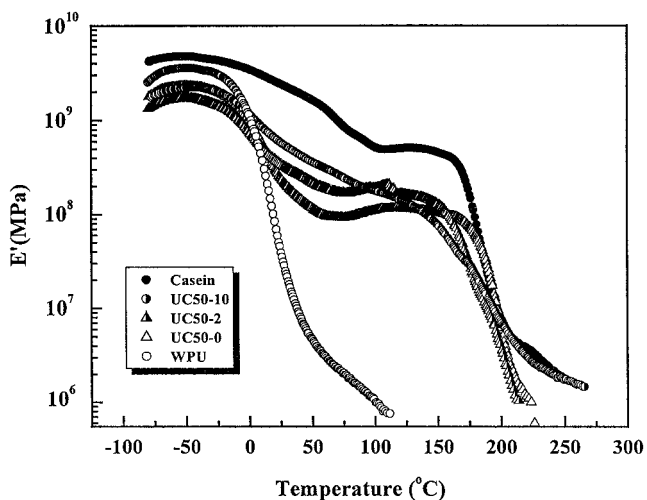


Figure 3 Dependency of storage modulus (E') on temperature for WPU, UC50-0, casein, UC50-2, and UC50-10 sheets.

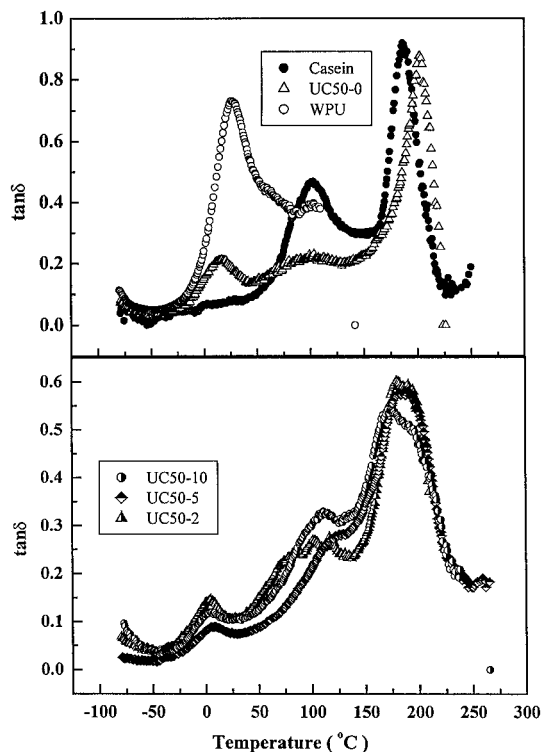


Figure 4 Dependency of $\tan \delta$ on temperature for WPU, UC50-0, casein, UC50-2, UC50-5, and UC50-10 sheets.

TABLE I
 T_g Data of the WPU, UC50-0, UC50-2, UC50-5, UC50-10,
 and Casein Sheets

Sheet	T_{g1} (°C)	T_{g2} (°C)	T_{g3} (°C)
WPU	25	—	—
UC50-0	20	102	202
UC50-2	2	101, 120	179, 189
UC50-5	5	125	190
UC50-10	2	112	175
Casein	—	100	187

polyurethane/nitrokonjac glucomannann semiinterpenetrating polymer networks.¹⁹ Therefore, the crosslinked component enhanced microphase separation between soft segments and hard segments of WPU, resulting in a decrease of T_g for WPU in the UC50-2, UC50-5, and UC50-10 sheets. Double $\tan \delta$ peaks of the crosslinked UC50-2 sheet at 101 and 120°C, respectively, were assigned to that of casein and crosslinked casein. As the ethanedial was further increased to 5 wt %, one $\tan \delta$ peak appeared at about 125°C, implying more completely crosslinked casein composition by ethanedial. In addition, double and shoulder $\tan \delta$ peaks of the UC50-2 sheets occurred at about 179 and 189°C, respectively, corresponding to T_{g3} for uncrosslinked and crosslinked components of casein in this case.

Physical and mechanical properties

TGA curves of the sheets are shown in Figure 5. The thermal decomposition of WPU sheet occurred between 264 and 370°C, which may be caused mainly by the breaking of urethane bonds. TGA curves of the sheets showed greatest weight loss in the temperature

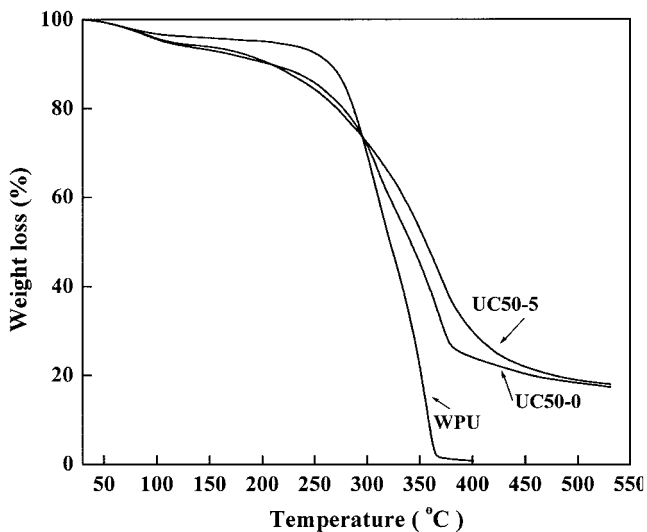


Figure 5 TGA curves of WPU, UC50-0, and UC50-5 sheets.

TABLE II
 Thermal Properties of WPU, UC50-0, and UC50-5 Sheets

Property	WPU	UC50-0	UC50-5
T_{sg} (°C)	264	267	276
T_{eg} (°C)	364	382	405
Weight loss (%)	91.7	61.3	60.5

range of 270–400°C, which were believed to be attributable to the intermolecular disintegration and breaking of the molecular structure.²⁰ The starting temperature of greatest thermal degradation and the values of the weight loss are listed in Table II. In view of these data, thermal stability was in the sequence UC50-5 > UC50-0 > WPU sheets. The higher thermal stability for UC50-5 sheets was caused by the occurrence of a network structure.

The mechanical properties are of primary importance for determining the performance of materials. The tensile strength (σ_b) and elongation at break (ϵ_b) of the sheets were plotted as a function of the ethanedial content in Figure 6. The tensile strength of the UC50-0 to UC50-10 sheets was higher than that of the WPU sheet, and reached a maximum value (20 MPa) at about 2–3 wt % of ethanedial content. The remarkable increase of the tensile strength of the UC sheets indicated that chemical crosslinking by adding ethanedial could increase the intermolecular interaction between WPU and casein to enhance the strength of the materials. Therefore, 2–3 wt % ethanedial in WPU/casein blends plays an important role in improving the mechanical properties of the sheets. However, when the ethanedial content was higher than 3 wt %, the tensile strength of the sheets decreased. This can be explained by the excessive ethanedial that led to the phase separation between WPU and casein. The elongation at break of the UC sheets decreased with increasing

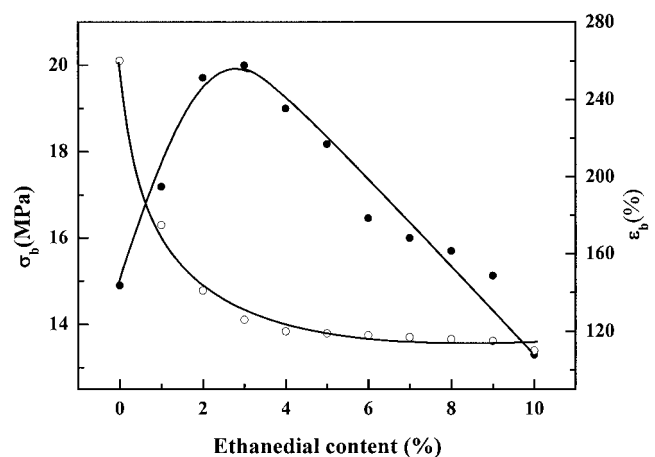


Figure 6 Dependency of σ_b (●) and ϵ_b (○) on ethanedial content for crosslinked UC50 sheets.

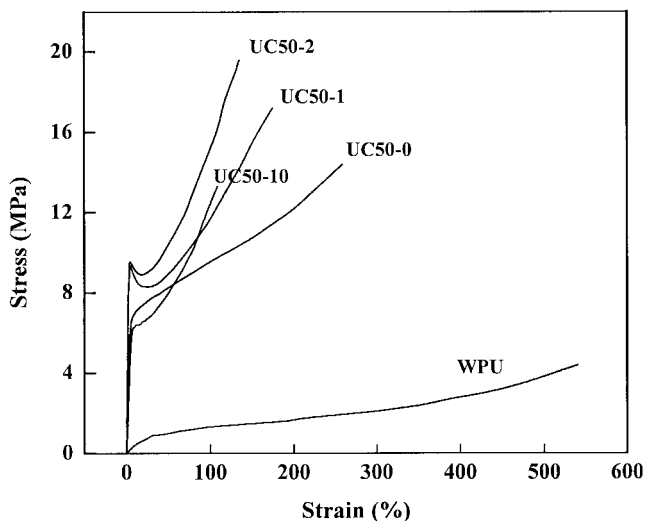


Figure 7 Stress-strain curves of the WPU, UC50-0, UC50-1, UC50-2, and UC50-10 sheets.

ethanedial content, which may be attributed to the difficulty of molecular motion caused by crosslinking.²¹ The stress-strain curves of the sheets are shown in Figure 7. The σ_b and ϵ_b values of the WPU sheets were 4.4 MPa and 539%, respectively, indicating its elastomeric characteristics. When WPU was blended with casein, the stress-strain curves exhibited a reinforced elastomer behavior. Interestingly, with an increase of the ethanedial, a yield point for sheets was observed, indicating a plastic characteristic. The area under the stress-strain curve can be used as a measurement of material toughness. The relatively large area of the UC50-0, UC50-1, and UC50-2 sheets indicated characteristics of toughened plastic, that is, enhanced strength and partly kept elongation.

With respect to the solubility test, the UC50-0 sheet was easily dissolved in water, so that the mechanical properties of this sheet in the wet state could not be obtained. However, the water resistivity of the crosslinked materials was significantly enhanced. The tensile strength and breaking elongation of the crosslinked UC50 series sheets in the wet state are shown in Figure 8. The σ_b of the crosslinked UC50-2 sheet achieved a maximum of 5 MPa, when the ethanedial content in the sheets was 2 wt %, and then decreased with increasing ethanedial content. The σ_b of the crosslinked UC50 sheets also decreased with an increase of ethanedial. This suggested that crosslinking reaction by inducing ethanedial could significantly improve the water resistivity of the sheets.

Figure 9 shows the dependencies of water absorption and weight loss on the ethanedial content for the sheets. A minimum of water absorption appeared in the curve, when the ethanedial content was 2 wt %, and then slowly increased with increasing ethanedial. The weight loss exhibited a trend similar to the water

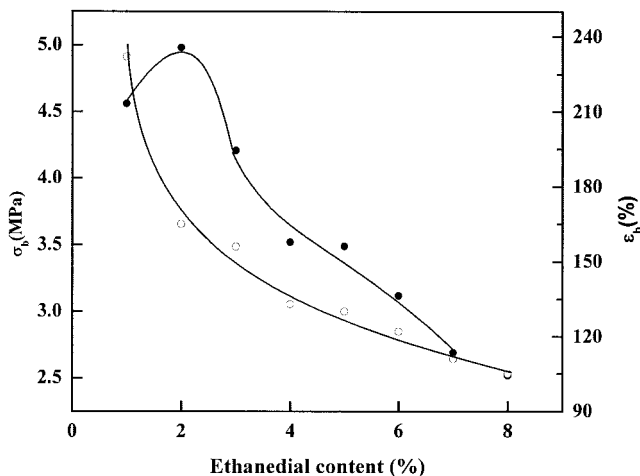


Figure 8 Dependency of σ_b (●) and ϵ_b (○) on ethanedial content for the crosslinked UC50 sheets in the wet state.

absorption behavior, suggesting that the water-soluble components increased with an increase of ethanedial. This can be explained that with an increase of ethanedial content, the crosslinking density increased to achieve a maximum at 2 wt % ethanedial and then slightly decreased because of excessive ethanedial, compared with $-NH_2$ groups in casein and the WPU chain, resulting in an increase of the uncrosslinked molecules. The dependency of the water absorption on time for the crosslinked UC50-2 sheets is shown in Figure 10. The water absorption increased very quickly initially to reach a maximum and then slowly decreased with an increase of time. After 30 min, the water absorption rate reached equilibrium approximately. When the sheets were immersed in water, water penetrated into the sheets, resulting in a limited swell (40%) and rapidly reaching equilibrium. How-

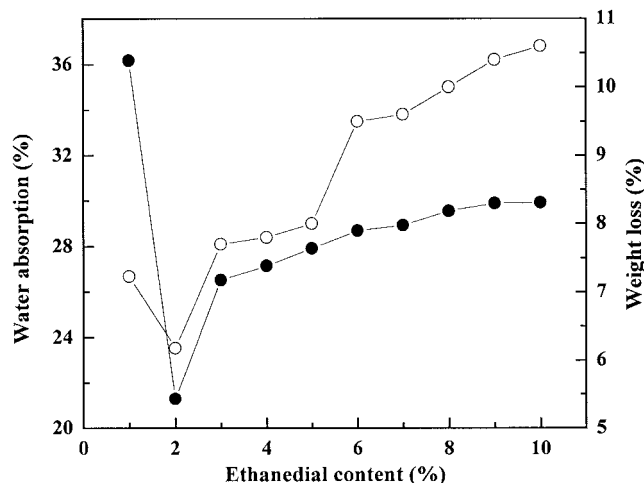


Figure 9 Dependency of water absorption (●) and weight loss (○) on the ethanedial content for the UC50 sheets.

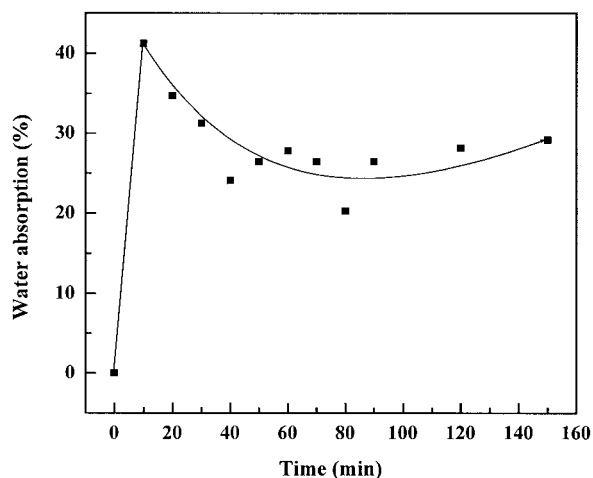


Figure 10 Dependency of the water absorption on immersing time for the crosslinked UC50-2 sheets.

ever, the water-soluble molecules in the sheets dissolved in water, leading to a decrease of the weight of the sheets.

CONCLUSIONS

The blends between WPU and casein exhibited in general a certain degree of miscibility. The sheets from blends of waterborne polyurethane and casein aqueous solution by crosslinking with ethanedial were successfully prepared. By inducing ethanedial into WPU/casein (1 : 1 by weight), the mechanical properties and water resistivity of the blend materials were enhanced

obviously, attributed to the crosslinking network. When the ethanedial content was about 2 wt %, the sheets showed significantly higher tensile strength, water resistivity, thermal stability, and partly kept elongation at break than those of uncrosslinked blends.

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