

# Structure–Properties Relationship of Starch/Waterborne Polyurethane Composites

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**ABSTRACT:** The blend materials from waterborne polyurethane (WPU)/starch (ST) with different contents (10–90 wt %) were satisfactorily prepared by using the solution casting method. Their miscibility, structure, and properties were investigated by wide-angle X-ray diffraction (WAXD), scanning electron microscope (SEM), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and the tensile tests, respectively. The results indicated that tensile strength of composite materials not only depended on the starch content, but also related to the microstructure of WPU. The sample WPU2 (1.75 of NCO/OH molar ratio) exhibited hard-segment order, but WPU1 (1.25 of NCO/OH molar ratio) had no hard-segment order. The appropriate starch filled into WPU not only de-

creased the ordered region of soft-segment matrix, but also hindered the formation of hard-segment ordered structure. The blend material from 80 wt % WPU1 and 20 wt % starch exhibited better tensile strength (27 MPa), elongation at break (949%), and toughness than others. With an increase of starch content, the WPU matrix with dispersed starch in the blends transitioned to dual-phase continuity and then to starch matrix with dispersed WPU. The results suggested that a certain extent of miscibility existed between WPU and starch in the blend materials on the whole composition ratio. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3325–3332, 2003

**Key words:** starch; waterborne polyurethane; blend

## INTRODUCTION

Biopolymer materials derived from renewable resources have been carried into the center of public interest for environmental protection and sustainable development. Thus, starch with multi-hydroxyl groups has been considered as a candidate material in certain yields because of its biodegradability, derivability, availability, and low cost.<sup>1</sup> However, the applications of pure starch materials are limited because of its water sensitivity and brittle property. Starch and its derivatives, in both granular and destructured form, have been blended with various plastics including polyethylene, poly(vinyl chloride), and olefin-based copolymers.<sup>2</sup> The thermoplastic blend materials are water-resistant, but not fully biodegradable. Recently, some natural polymers, such as cellulose whiskers and derivatives,<sup>3,4</sup> industrial lignin,<sup>5,6</sup> soy protein,<sup>7</sup> and poly(lactic acid),<sup>8</sup> have been induced into starch to obtain the fully biodegradable materials. In

these blend systems, starch and its derivatives with relatively higher rigidity play a role as a modulus-modifier, extender, gas barrier, etc.

Now, the development of waterborne polyurethane (WPU) has become the trend of polyurethane materials because of environmental requirements.<sup>9</sup> Thus WPU can be used to improve the properties of starch sheets by the blend method. In our laboratory,<sup>10,11</sup> the WPU/starch blend sheets have been prepared by the compression-molding and solution-casting methods, respectively. Although there is no free isocyanate to react with starch in the WPU/starch blends, certain miscibility between WPU and starch is possible to enhance the tensile strength and the elongation of the blends. To exploit the materials further, a basic understanding of the effect of NCO/OH ratio in WPU and starch content on microstructure as well as properties of the blend materials is essential.

In this work, two kinds of WPU with different ordered structures were synthesized by changing the NCO/OH molar ratio, and then mixed with starch in aqueous system to obtain the blend sheets by solution casting. The effect of starch content on morphology, miscibility, and thermal and mechanical properties of the blends were investigated by wide-angle X-ray diffraction (WAXD), scanning electron microscope (SEM), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and the tensile tests.

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## EXPERIMENTAL

### Materials

All the chemical reagents used were analytically pure and obtained from commercial sources in China. Corn starch was purchased from Wuhan Starch Co. (China). 2,4-Toluene diisocyanate (TDI) was purchased from Jiangbei Chemical Reagents Factory (Wuhan, China). Polyethylene-propylene adipate glycol (PEPA) with number-average molecular weight ( $M_n$ ) of 1980 was a gift of Guangzhou Chemistry Institute of China Academy. Dimethylol propionic acid (DMPA) and triethylamine (TEA) were obtained from Chengdu Polyurethane Co. and Shanghai Chemical Co. (China), respectively.

TDI was redistilled before use. PEPA and DMPA were vacuum-dried before use. TEA and butanone were treated with 3 Å molecular sieves to dehydrate. Starch was vacuum-dried at 105°C for 5 h before use.

### Synthesis of WPU

To synthesize WPU dispersions, PEPA and DMPA were introduced into a four-necked flask equipped with mechanical stirrer and thermometer, and then heated for melting at 80°C; then TDI was added drop by drop. The reaction was carried out at dry nitrogen atmosphere for 2–3 h until the —NCO groups content reached a given value, which was determined by the method of dibutylamine back titration. Subsequently, the butanone was poured into the flask to reduce the viscosity of prepolymer and then cooled to 60°C. After neutralized with TEA for 30 min, the product was dispersed with distilled water and solid content was controlled to 25 wt % under vigorous stirring for 30 min. Two kinds of WPU with 1.25 and 1.75 of NCO/OH molar ratio were synthesized; their compositions are listed in Table I.

### Preparation of blends

The 5 wt % starch aqueous was heated slowly up to 80°C with vigorous stirring for 1 h to obtain a trans-

**TABLE I**  
Compositions of Waterborne Polyurethane with Different NCO/OH Molar Ratios

Sample	Polyols (mol)		TEA (mol)	TDI (mol)	NCO/OH molar ratio
	PEPA	DMPA			
WPU1	0.025	0.025	0.025	0.063	1.25
WPU2	0.025	0.025	0.025	0.088	1.75

*Note.* The molar ratio among PEPA, DMPA, and TEA was held constant as 1 : 1 : 1.

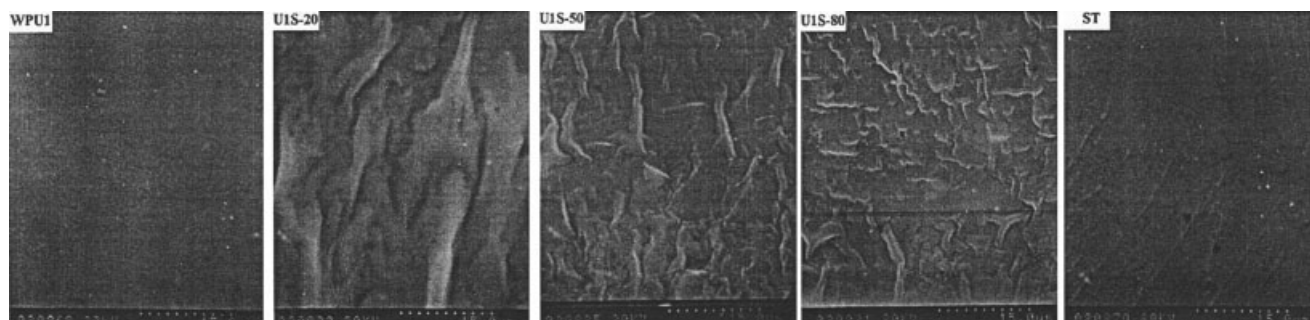
lucent paste of starch. Subsequently, the WPU solution was added into the starch paste and stirred for 30 min. Last, the mixture was degassed and then cast on a Teflon plate mold, followed by drying at 40°C in an oven for 10 h to obtain a transparent sheet. The thickness of sheet was controlled to be about 0.1 mm. According to ISO/R4831966 (E), all the sheets were stored at room temperature and 75% relative humidity for 2 weeks to make the moisture content in the sheet about 5–13% before characterization.

The blend sheets prepared from WPU1 and WPU2 were coded as U1S and U2S. At the same time, by changing the starch content to be 10, 20, 30, 40, 50, 60, 70, 80, and 90 wt %, the blend materials were coded as U1S-10-U1S-90 as well as U2S-10-U2S-90, respectively. In addition, the sheet prepared from pure starch was coded as ST.

### Characterization

WAXD patterns of the sheets were recorded on D/max-1200 X-ray diffractometer (Rigaku Denki, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5405 \times 10^{-10}$  m), and the samples were examined with  $2\theta$  ranging from 4 to 40° at a scanning rate of 4° min<sup>-1</sup>.

SEM micrographs were taken on a Hitachi S-570 microscope (Japan). The sheets were frozen in liquid nitrogen and snapped immediately, and the cross sections of the sheets were coated with gold for SEM observation.



**Figure 1** SEM micrographs of cross section for WPU1, ST, and U1S sheets with various weight ratios of starch.

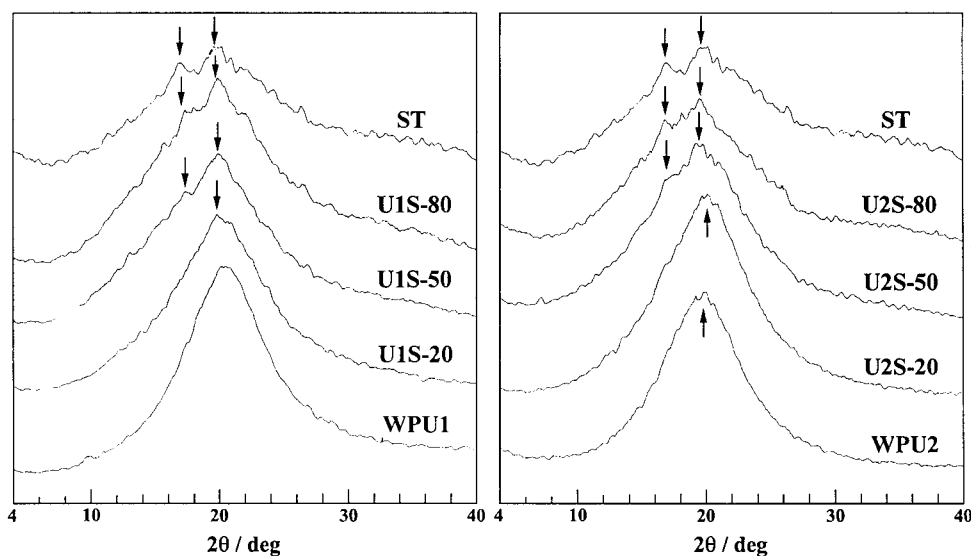


Figure 2 WAXD patterns of sheets of WPU1, WPU2, ST, and the blends.

DSC was carried out on a DSC-204 apparatus (Netzsch Co., Germany) under a nitrogen atmosphere at a rate of  $10^{\circ}\text{C min}^{-1}$  from  $-140$  to  $230^{\circ}\text{C}$ . Prior to the test, the samples were heated from the room temperature to  $100^{\circ}\text{C}$  to remove moisture and other volatile components in the sheets and then cooled to  $-140^{\circ}\text{C}$  at a rate of  $20^{\circ}\text{C min}^{-1}$ .

DMTA was carried out by using a DMTA-V dynamic mechanical analyzer (Rheometric Scientific Co., USA) at a frequency of 1 Hz in the temperature range from  $-80$  to  $50^{\circ}\text{C}$  with a heating rate of  $5^{\circ}\text{C min}^{-1}$ .

The tensile tests of the sheets were measured on a universal testing machine (CMT6502, Shenzhen SANS Test Machine Co. Ltd., China) with a tensile rate of  $5 \text{ mm min}^{-1}$  according to ISO6239-1986 (E).

## RESULTS AND DISCUSSION

### Morphology of the blends

Figure 1 shows the SEM micrographs of cross section of the WPU1, ST, and blend sheets. The fracture surface of WPU1 and ST sheets are smooth and flat. However, the U1S-20 sheet blended with 20 wt % starch exhibited a coarse and fluctuant fracture surface, indicating that the starch was separated into WPU matrix. When the content of starch increased up to 50 wt %, the blend achieved dual continuous phases. As regards to U1S-80 sheet containing 80 wt % starch, the smaller fiber-like objects dispersed into the flat background, indicating a structure of starch matrix with dispersed WPU. Consistent with most cases, the

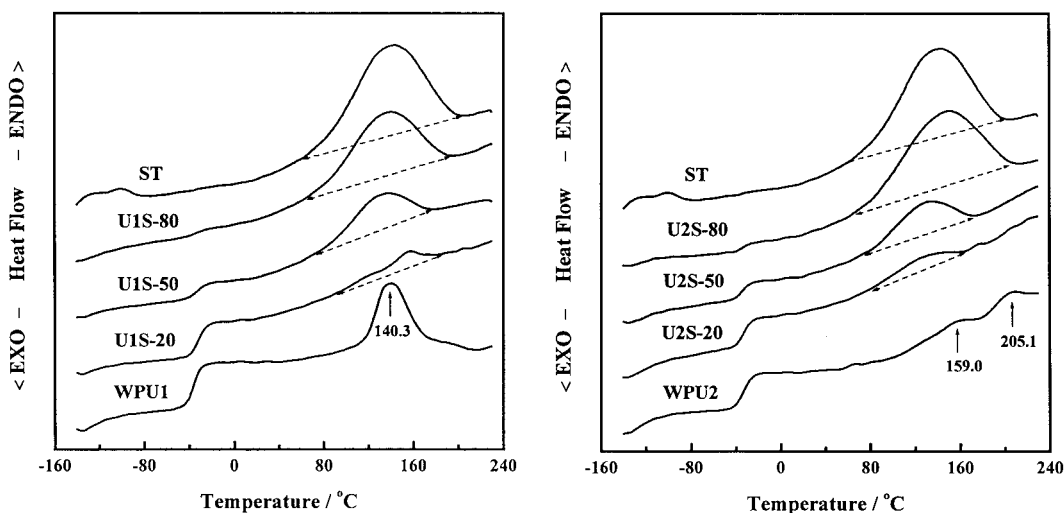


Figure 3 DSC thermograms of WPU1, WPU2, ST, and the blends.

TABLE II  
Glass Transition Temperature and  $\alpha$  Transition Assigned to Soft-Segment for WPU1, WPU2, and their Blends with Starch of Various Contents Measured by DSC and DMTA

	WPU types	Starch content (wt %)			
		0	20	50	80
$T_g$ (onset)/°C	WPU1	-42.6	-38.9	-41.3	-43.2
	WPU2	-41.1	-39.5	-40.9	-40.7
$\Delta C_{p,g}/\times 10^2 \text{ J g}^{-1} \text{ K}^{-1}$	WPU1	0.46	0.32	0.15	0.06
	WPU2	0.38	0.27	0.18	0.08
$T_\alpha$ /°C	WPU1	-20.83	-18.01	-25.33	-25.39
	WPU2	-29.32	-27.28	-29.02	-31.01
Height of tan $\delta$ peak	WPU1	0.55	0.12	0.12	0.13
	WPU2	0.28	0.23	0.11	0.06

major component of the blend formed the continuous phase, whereas the minor component formed the dispersed phase without obvious phase separations.

WAXD patterns for two series of blends are shown in Figure 2. The peaks at 17 and 19.5° assigned to the crystalline peaks of starch, which weakened obviously with a decrease in the starch content. The US-20 containing 20 wt % starch exhibited the amorphous patterns, similar to the corresponding WPU, indicating that the starch dispersed into WPU matrix could not form the domain independently. However, the crystalline peak of the blends with relatively high starch content (e.g., 50 and 80 wt %) appeared in 17 and 19.5°, suggesting that starch in the blends aggregated to form the order domains and kept the crystalline behavior in ST.

DSC thermograms in Figure 3 gave the detailed information of one glass transition assigned to WPU;

the data are listed in Table II. The blends containing 20 wt % starch exhibited higher glass transition temperature ( $T_g$ ) than the corresponding WPU and the other blends with starch content of higher than 50 wt %, suggesting that US-20 sheets exhibited relatively higher miscibility. Usually, the miscibility in the blend resulted from the specific interaction between the components, such as hydrogen bonding between carbonyl of WPU and hydroxyl of starch in this case. Figure 4 showed that the changes of heat capacity ( $\Delta C_{p,g}$ ) decreased with an increase of starch content, and the relationship of  $\Delta C_{p,g}$  versus starch content for the sheets U1S and U2S series was not linear, indicating that there was some interaction between WPU and starch.<sup>12</sup> DMTA can be used to reflect the mobility of chain segment and to obtain the temperature of  $\alpha$ -relaxation ( $T_\alpha$ ) corresponding to  $T_g$  from DSC. Usually the  $T_\alpha$  was higher up to 10°C than  $T_g$  from DSC

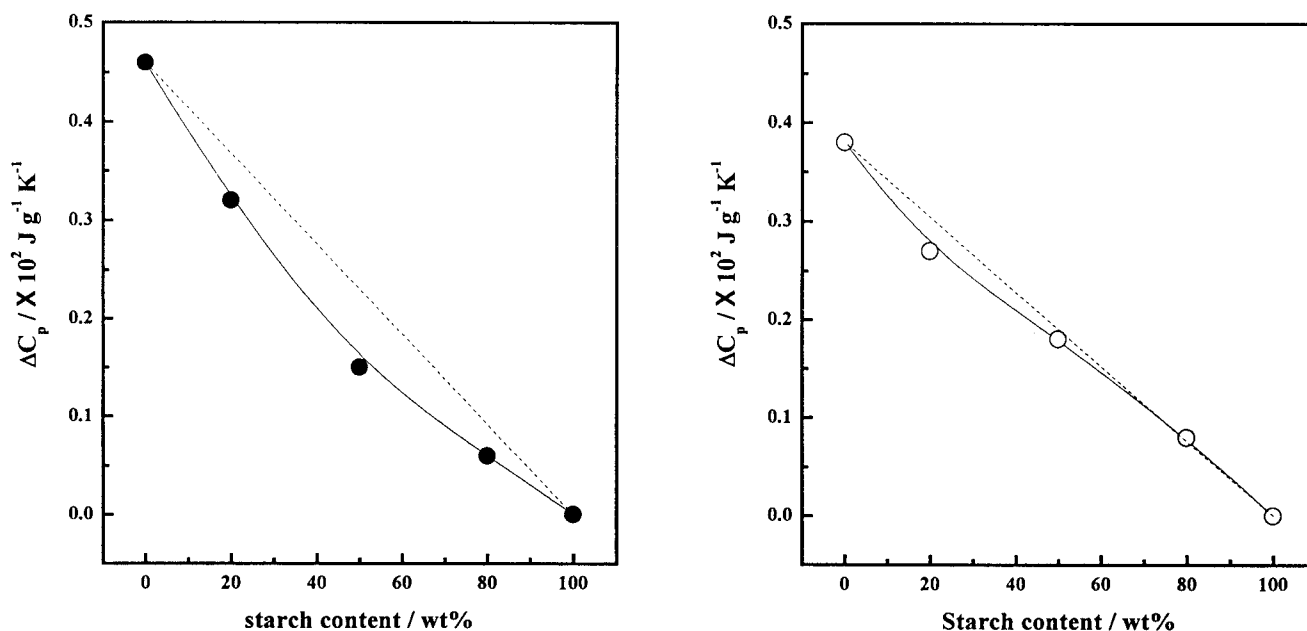


Figure 4 Dependence of heat capacity ( $\Delta C_p$ ) determined by DSC on starch content for U1S (●) and U2S (○) series sheets.

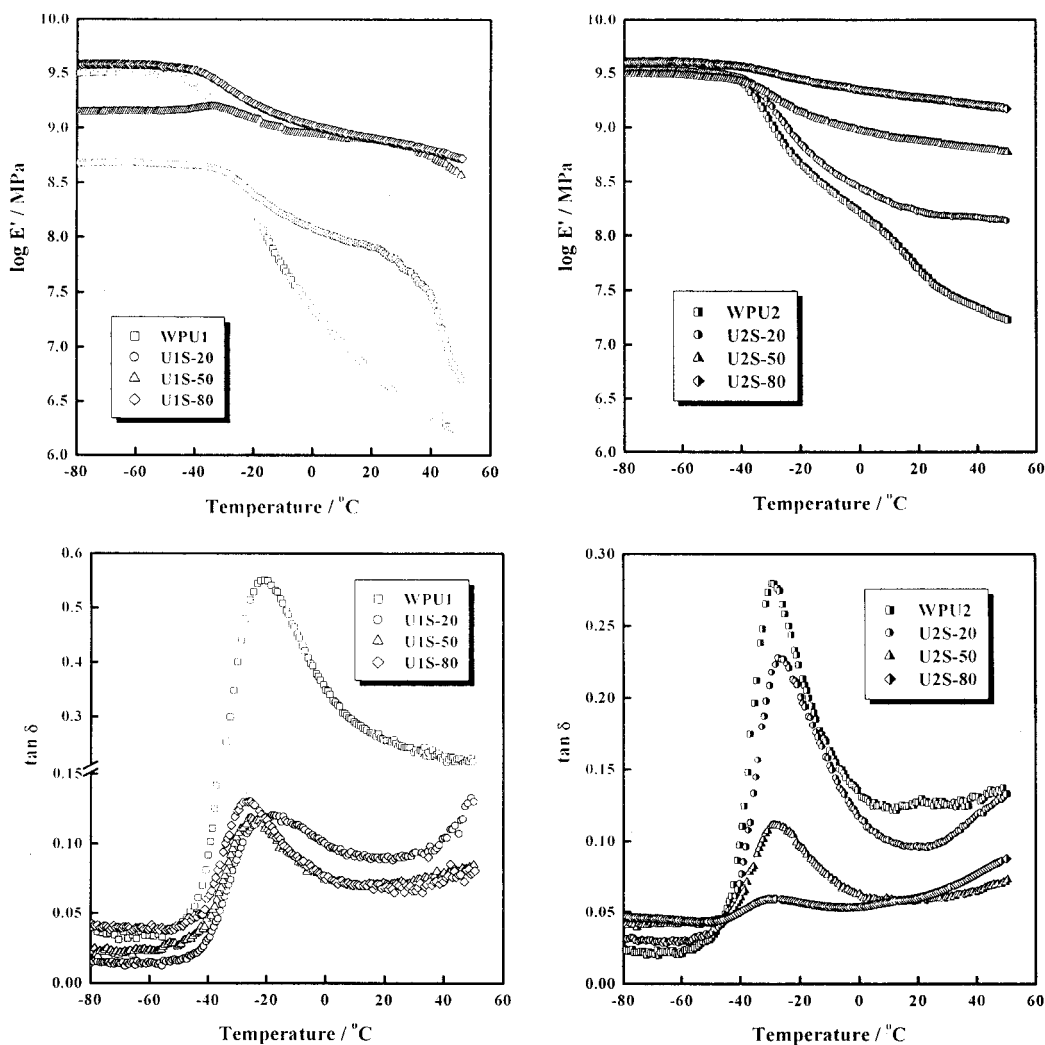


Figure 5 DMTA curves of the sheets WPU1, WPU2, ST, and the blends.

because of the dynamic nature of the DMTA test.<sup>13</sup> As shown in Table II,  $T_{\alpha}$  of US-20 sheets obtained from Figure 5 were higher than corresponding WPU sheets, suggesting that the mobility of soft segment assigned to WPU was restricted because of the interaction between WPU and starch. When the starch content increased, the starch domains formed, reducing the intermolecular interaction between WPU and starch.

#### Microstructure of the blends

DSC usually reflects the greater scale of molecular mobility than DMTA and mainly focused on the purity of soft-segment matrix or the mixing degree of soft and hard segment. Thus, the differences of  $T_g$  values for two series of WPU were very weak, indicating that the changes of NCO/OH molar ratio in WPU had no influence on the aggregation of soft segment. DSC thermograms in Figure 3 showed that WPU1 had one

melting peak at 143.3 $^{\circ}\text{C}$  assigned to the order of soft segment, but WPU2 exhibited two melting peaks at 159.0 and 205.1 $^{\circ}\text{C}$  assigned to the order of soft segment and the order of hard segment, respectively.<sup>14</sup> It indicated that the increase of NCO/OH molar ratio decreased the order of soft segment, but enhanced the order of hard segment. The obvious difference of  $T_{\alpha}$  for two series blends suggested the freedom of soft-segment mobility was mainly restricted by the ordered structure in soft-segment matrix, and thus WPU1 with more ordered structure of soft segment exhibited higher temperature of  $\alpha$ -transition. Compared with WPU, higher  $T_{\alpha}$  of US-20 sheets implied that the starch in the soft-segment matrix of WPU restricted the mobility of soft segment because of the relatively strong hydrogen-bonding interaction. However, when the starch content was over 50 wt %, the starch domain formed and exhibited relatively weak interaction with WPU, resulting in the lower  $T_{\alpha}$  (e.g., US-50 and US-80 sheets).

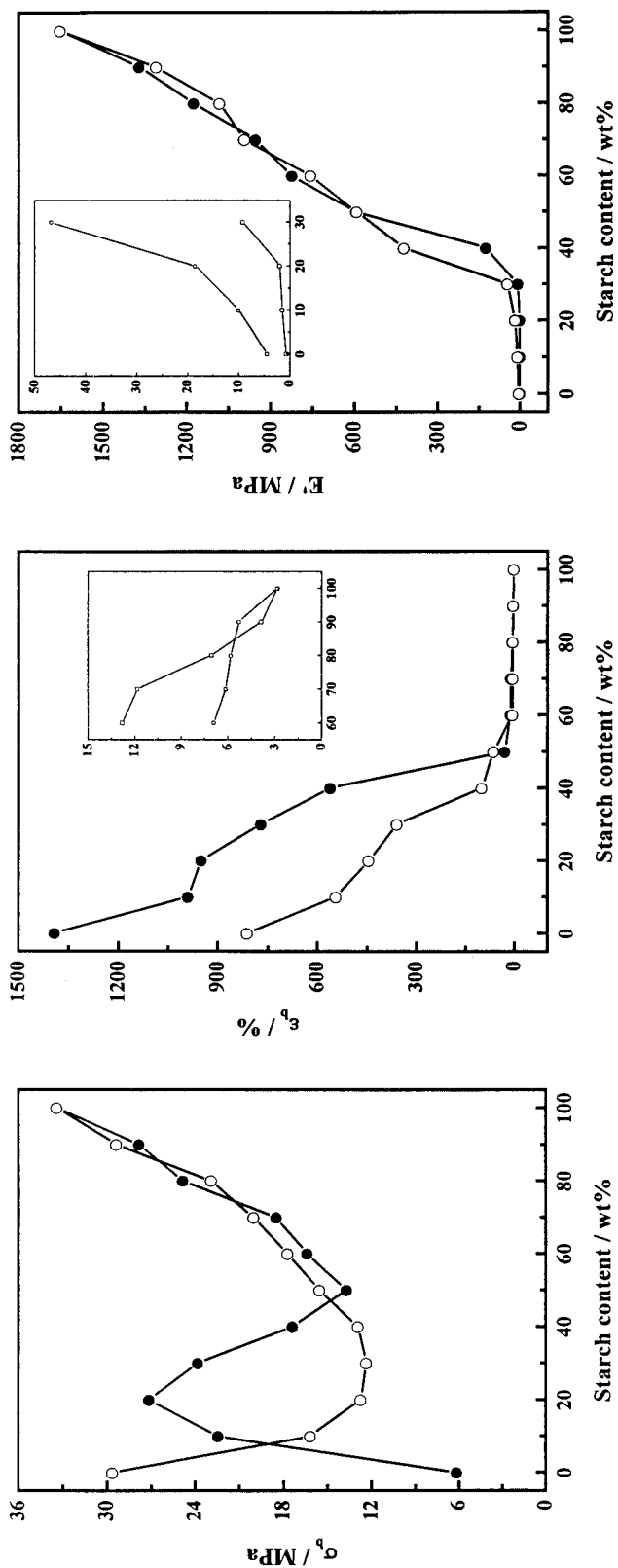


Figure 6 Tensile strength ( $\sigma_b$ ), elongation at break ( $\epsilon_b$ ), and Young's modulus ( $E'$ ) as a function of starch content for U1S (●) and U2S (○) series sheets.

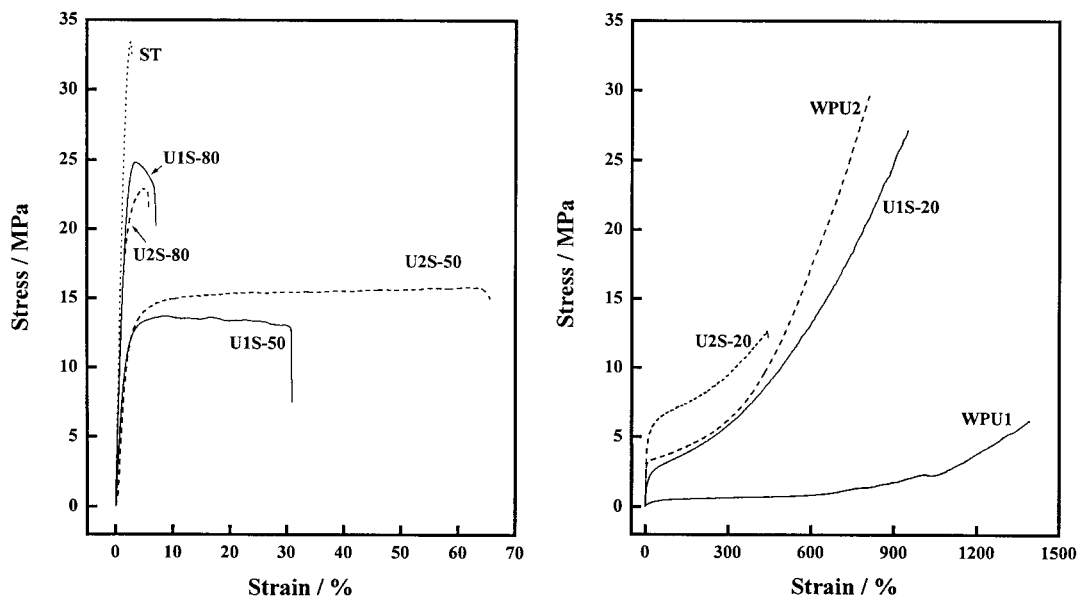


Figure 7 Stress-strain curves of WPU1, WPU2, ST, and two series of the blend containing 20, 50, and 80 wt % starch.

The range and shape of melting transition may indicate the effects of incorporating starch on the structure of WPU. Compared with the DSC thermograms of the corresponding WPU, the ordered structure in US-20 sheets was destroyed, which can be seen by the weakening of melting peak assigned to the ordered soft segment in U1S-20 and the disappearance of melting peak at high temperature for the ordered hard segment in U2S-20. Although the DSC curves of US-20 in two series were very similar, their changes compared to origin WPU were very different. The starch just only reinforced the soft segments in U1S-20, but for U2S-20, it also destroyed the order of hard segments. With an increase of starch content, the endothermic peak gradually broadened and strengthened, and even that of US-80 sheets containing 80 wt % starch were very similar to ST sheet, indicating that the increase of starch content resulted in the expansion of the ordered starch domain. This is in good agreement with the sole crystalline behavior of starch shown in Figure 2, when the starch content is relatively higher.

### Mechanical properties

The experimental results of the tensile strength, elongation at break, and Young's modulus for two series blends are shown in Figure 6 with the magnifying figure in the insert. Usually, the incorporation of starch as a relatively rigid granule in polymeric blend result in a decrease of elongation at break and tensile strength,<sup>15,16</sup> but an increase of modulus.<sup>17</sup> The changes of elongation at break and Young's modulus were consistent with the behaviors of other starch/

polymer systems. However, the tensile strength of U1S series first increased to 20 wt % starch content and then decreased to 50 wt % starch content, followed by constantly increasing up to pure ST sheet. Simultaneously, the tensile strength of U2S series first decreased up to 30 wt % starch content, and then constantly increased up to pure ST sheet. When the starch content was higher than 50 wt %, the mechanical properties for the two series were very close because the starch continuous phase dominated the mechanical properties of blends. When the starch content was lower than 50 wt %, the difference of tensile strength for two series of blends appeared, owing to the effects of starch on the microstructure of WPU. WPU2 with higher NCO/OH molar ratio exhibited higher tensile strength than WPU1 because of the formation of hard-segment ordered structure. Thus, the incorporation of rigid starch with moderate content not only filled into the soft-segment matrix to reinforce the materials, but also hindered the formation of hard-segment ordered structure to result in the decrease of tensile strength, resulting in the increase of tensile strength of WPU with relatively low NCO/OH molar ratio.

Stress-strain curves of WPU1, WPU2, ST, and the blends with different WPU and starch contents are shown in Figure 7. The ST and the blend sheets containing 80 wt % was very rigid and brittle. However, the flexibility of the blend sheets containing 50 wt % WPU enhanced slightly, but its brittleness was not obviously improved. When the starch content decreased to 20 wt % in U1S series, the composite material exhibited better flexibility and tough properties than others. The stress-strain curves obviously indicated that the U1S-20 sheet has simultaneously good

$\sigma_b$  (27 MPa) and  $\epsilon_b$  (949%), as well as relatively large area under the stress–strain curve, which represents the material toughness. The reinforcement of 20 wt % starch in WPU1 plays an important role in improving the mechanical properties of the blend material U1S-20.

### CONCLUSION

Blend materials were prepared successfully from two kinds of WPU with different NCO/OH molar ratios and starch with different contents by solution casting. The certain extent of miscibility occurred between WPU and starch in the blend materials on the whole ratio of WPU to starch. With an increase of starch content, the WPU matrix with dispersed starch in the blends changed to dual-phase continuity, and finally to starch matrix with dispersed WPU. Compared to the blends containing WPU2 (1.75 of NCO/OH molar ratio), the blends containing WPU1 (1.25 of NCO/OH molar ratio) and 20 wt % starch exhibited significantly good tensile strength, elongation at break, and toughness. Therefore, 20 wt % starch in WPU1 plays an important role in improvement of various mechanical properties of the blend materials.

### References

1. Whistler, R. L. in *Starch: Chemistry and Technology*; Whistler, R. L.; Bemiller, J. N.; Paschall, F. F., Eds.; Academic Press: New York, 1984.
2. Chandra, R.; Rustgi, R. *Prog Polym Sci* 1998, 23, 1273.
3. Anglès, M. N.; Dufresne, A. *Macromolecules* 2001, 34, 2921.
4. Amass, W.; Amass, A.; Tighe, B. *Polym Int* 1998, 47, 89.
5. Baumberger, S.; Lapierre, C.; Monties, B.; Lourdin, D.; Colonna, P. *Ind Crops Prod* 1997, 6, 253.
6. Baumberger, S.; Lapierre, C.; Monties, B.; Della Valle, G. *Polym Degrad Stab* 1998, 59, 273.
7. Huang, H. C.; Chang, T. C.; Jane, J. *JAACS* 1999, 76, 1101.
8. Martin, O.; Avèrous, L. *Polymer* 2001, 42, 6209.
9. Noble, K. L. *Prog Org Coat* 1997, 32, 131.
10. Wu, Q.; Zhang, L. *Ind Eng Chem Res* 2001, 40, 558.
11. Wu, Q.; Zhang, L. *J Appl Polym Sci* 2001, 79, 2006.
12. Huang, M.; Kuo, S.; Wu, H.; Chang, F.; Fang, S. *Polymer* 2002, 43, 2479.
13. Gao, S.; Zhang, L. *Macromolecules* 2001, 34, 2202.
14. Xiu, Y. Y.; Zhang, Z. P.; Wang, D. N.; Ying, S. K.; Li, J. X. *Polymer* 1992, 33, 1335.
15. St-Pierre, N.; Favis, B. D.; Ramsay, J. A.; Verhoogt, H. *Polymer* 1997, 38, 647.
16. Lim, S-T.; Lin, J. J.; Rajagopalan, S.; Seib, P. A. *Biotechnol Prog* 1992, 8, 51.
17. Vaidya, U. R.; Bhattachaya, M.; Zhang, D. *Polymer* 1995, 36, 1179.