

# Semi-Interpenetrating Polymer Networks from Castor Oil-Based Polyurethane and Nitrokonjac Glucomannan

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**ABSTRACT:** New semi-interpenetrating polymer networks (semi-IPNs) coded as PUNK were successfully synthesized from castor oil-based polyurethane (PU) prepolymer and 10–40 wt % nitrokonjac glucomannan (NKGM) containing a degree of substitution of 2.4 and a weight-average molecular weight of  $4.75 \times 10^4$ . The semi-IPN sheets that were 100  $\mu\text{m}$  thick were cured more speedily than PU, with curing times of 5 h for PUNK and 16 h for PU at 50–70°C. The structure and miscibility of the semi-IPN sheets were studied by Fourier transform infrared spectroscopy, ultraviolet spectroscopy, and scanning electron microscopy. The results showed that a strong intermolecular interaction caused by hydrogen bonding between NKGM and PU exists in PUNK, resulting in good miscibility. When the NKGM content of the semi-IPNs sheets was 20 wt %, the tensile strength and light transmittance were obviously higher than that of the PU sheets. The NKGM in the semi-IPN sheets plays an important role not only in accelerating the cure but also in improving the mechanical properties and biodegradability. As a new material prepared from renewable resources, PUNK has potential applications because of its biodegradability. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2076–2083, 2001

**Key words:** nitrokonjac glucomannan; polyurethane; synthesis; semi-interpenetrating polymer network; mechanical property; miscibility; biodegradable material

## INTRODUCTION

In recent decades polymer blends have continued to be a subject of intensive investigation in both industrial and academic domains because of the simplicity and effectiveness of mixing two different polymers to obtain new materials.<sup>1</sup> Interpenetrating polymer networks (IPNs)—a mixture of two or more crosslinked polymers—is mutual

blend held together by permanent entanglement.<sup>2</sup> IPN materials have drawn much attention because of their special properties, which result from the interlocking of the polymer chains.<sup>3</sup> Polyurethane (PU) has been widely used as one of the individual polymers possessing network structure owing to its good flexibility and elasticity. A lot of work concerning IPNs has been reported by Sperling et al.,<sup>4,5</sup> Frisch et al.,<sup>6,7</sup> and Hourston et al.<sup>8,9</sup> Interestingly, castor oil, a natural vegetable oil, has been used as a polyol for the synthesis of the PU phase in IPNs because of its three reactive hydroxyl groups.<sup>10</sup> Castor oil-based PU–poly (ethyl methacrylate) IPNs as tough sheets,<sup>11</sup> PU–polystyrene semi-IPNs as tough plastics and reinforced elastomers,<sup>12</sup> and

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PU–epoxy grafted IPNs<sup>13</sup> have all been investigated and found to yield enhanced properties.

Recently, naturally occurring polysaccharides have been reevaluated as renewable resources because they are environmentally friendly substances and possess potentials for industrial, agricultural, and medical applications as substitutes for some petrochemical products.<sup>14</sup> In a recent work we successfully prepared and characterized coatings on regenerated cellulose films by using grafted or semi-IPNs materials from castor oil-based polyurethane and natural polymers such as nitrocellulose,<sup>15</sup> elaeostearin,<sup>16</sup> and depolymerized chitosan.<sup>17</sup> This showed<sup>18</sup> that a shared PU network crosslinks simultaneously with cellulose and that IPN coating occurs in these compound sheets, resulting in the enhancement of mechanical properties and the transmitting of light. More important, the biodegradability of these IPN-coated sheets was investigated, and the results indicated that they were degraded by microorganisms in soil, accompanied by the production of CO<sub>2</sub>, H<sub>2</sub>O, glucose cleaved from cellulose, aromatic ethers from PU, and other products.<sup>19</sup> It is well known that konjac glucomannan (KGM), a natural polysaccharide with a main chain of a  $\beta$ -1,4-pyranoside bond linked to mannose and glucose,<sup>20</sup> has been widely used in the food industry as a thickening, stabilizing, and gelling agent because of its unique rheological properties.<sup>21</sup> Recently, the study of KGM for applications in chemical engineering and medicine has attracted attention.<sup>22</sup> It is worth noting that konjac glucomannan is also a renewable, nontoxic, and low-cost resource that has the potential to be utilized in the preparation of new IPN materials for a “green” chemical industry.

In this work nitrokonjac glucomannan (NKGM) was prepared from konjac glucomannan. An attempt was made to prepare novel semi-interpenetrating polymer networks according to Hourston's view<sup>23</sup> by using NKGM, a linearly structural polymer, with polyurethane prepolymer synthesized from castor oil and toluene diisocyanate. Using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), tensile testing, and ultraviolet spectroscopy (UV), we studied the structure, morphology, and thermal and mechanical properties, as well as the optical transmittance of this material.

## EXPERIMENTAL

### Materials

All chemical reagents used were of analytical grade. Castor oil was chemically pure, and konjac glucomannan was commercially purchased in China. Castor oil and toluene diisocyanate (TDI) were redistilled under reduced pressure to dehydrate before use. The following method was used to obtain konjac glucomannan (KGM) from plant tubers of *Amorphophallus konjac* (supplied by the Zhuxi Konjac Institute, Hubei, China), a cheap agricultural crop in China. The konjac tubers were sliced into pieces about 5 mm thick, dried in sunlight for a week, and then pulverized by a mill. The crude flour was immersed in 70% (v/v) methanol for 30 min and then dried at 60°C under reduced pressure. The dried flour was extracted with benzene–absolute alcohol (4:1 v/v) and trichloromethane–*n*-butanol mixtures (Sevag method) for 48 h to remove fat and protein, respectively. The product was dissolved in 6% H<sub>2</sub>O<sub>2</sub> at 30°C for 30 min, then stirred vigorously for 2 h. Enough acetone was added to the mixture solution to obtain a white-cotton-like precipitate, namely, crude konjac glucomannan, which was filtered, compressed, and dried at 40°C for 12 h. The konjac glucomannan was dissolved in water to prepare a concentration of 2 wt %. Subsequently, KAl(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O ( $W_{\text{KGM}}/W_{\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O}} = 10:1$ ) and isopropanol were used for further purification in order to obtain powdered konjac glucomannan. The viscosity-average molecular weight ( $\bar{M}_v$ ) of the konjac glucomannan was determined by viscometry to be  $9.5 \times 10^5$  according to  $[\eta] = 6.37 \times 10^{-4} M^{0.74}$  at 30°C in water.<sup>24</sup>

### Preparation of Nitrokonjac Glucomannan

In a round-bottomed flask equipped with a mechanical stirrer were added 4 g of KGM and a mixture of 100 g of fuming nitric acid, 10 g of sulfuric acid, and 40 g of P<sub>2</sub>O<sub>5</sub>. The flask was placed in an ice-water bath and cooled for 2 h. Then the reaction was controlled at 20°C for 2 days. The resulting solution was poured into excess water to precipitate the nitrokonjac glucomannan (NKGM). This crude product was dissolved with acetone and then was precipitated and washed 3 times with water. After vacuum-drying at 50°C for 8 h, 3.1 g of white powdered NKGM was obtained. The elemental analysis of KGM and NKGM was performed using an element ana-

**Table I Results of Element Analysis of KGM and NKGM**

Elements	C	H	O	N
KGM	42.16	7.93	49.91	—
NKGM	25.37	2.63	59.52	12.48

lyzer (MOD-1106, Carlo Erba Strumentazione, Italy). The results are listed in Table I, and the average degree of substitution of NKGM (DS) was calculated by

$$DS = \frac{162 \times w_N}{14 - 45 \times w_N} \quad (1)$$

where  $w_N$  is the weight percentage of nitrogen. The DS value of NKGM was found to be 2.4. The FTIR spectra of KGM and NKGM are shown in Figure 1. The broad stretching band of —OH groups around  $3357 \text{ cm}^{-1}$  for KGM was sharply decreased in the spectrum of NKGM, indicating that the hydrogen atoms of —OH groups in KGM were substituted by —NO<sub>2</sub> groups. Accordingly, the three obvious absorption bands, at  $1660 \text{ cm}^{-1}$ ,  $1281 \text{ cm}^{-1}$ , and  $835 \text{ cm}^{-1}$ , were assigned to the —ONO<sub>2</sub> groups,<sup>25</sup> indicating that water-insoluble nitrokonjac glucomannan had been synthesized.

The weight-average molecular weight ( $M_w$ ) of nitrokonjac glucomannan was determined by using a DAWN-DSP multiangle laser photometer (Wyatt Technology Co., Santa Barbara, CA, USA) combined with a pump P100 (Thermo Separation Products) equipped with a TSK-GEL G4000 HHR column ( $7.8 \text{ mm} \times 300 \text{ mm}$ ) and a differential refractive index detector (RI-150) at  $25^\circ\text{C}$ . The refractive index increment ( $dn/dc$ ) of the nitrokonjac glucomannan in THF, measured with a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co.) at  $633 \text{ nm}$  and  $25^\circ\text{C}$ , was 0.093. Astra software was utilized for data acquisition and analysis. The  $M_w$  of NKGM was determined to be  $4.75 \times 10^4$ , and its polydispersity ( $M_w/M_n$ ) was 1.7.

### Preparation of PU–NKGM

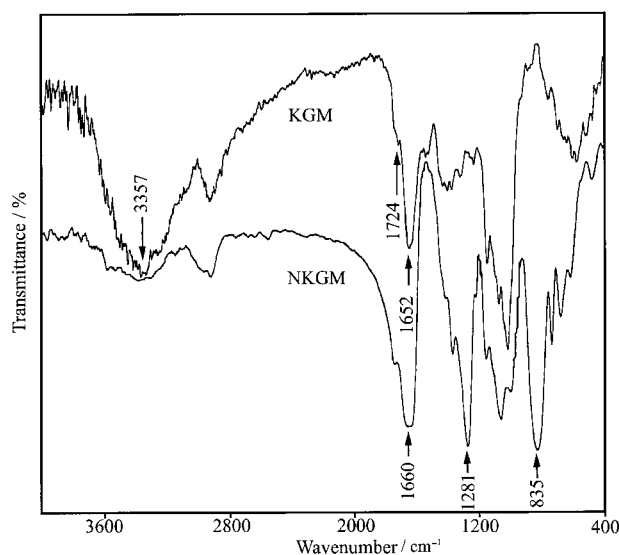
A three-necked flask was fitted with a nitrogen inlet tube, a stirrer, and a pressure-equalizing dropping funnel. Then 29 g of TDI was poured into the flask, after which 57 g of castor oil was dropped into it under a nitrogen atmosphere at  $40^\circ\text{C}$ . This addition was completed within 50 min,

and then the stirring was maintained at  $60^\circ\text{C}$  for 1.5 h to produce the PU prepolymer.

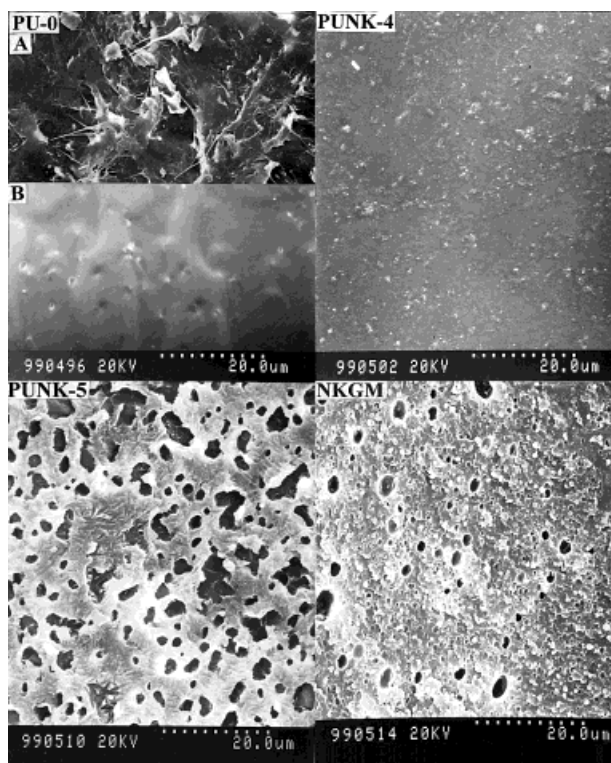
The value of  $[\text{NCO}]/[\text{OH}]$  was predetermined theoretically to be 1.08. Therefore, in tetrahydrofuran (THF) at room temperature, 3 g of PU prepolymer was mixed with the desired weight of NKGM, 0.226 g of 1,4-butanediol (BD) as a chain-extending agent, and 0.06 g of diethylenetriamine (DETA) as a catalyst. The resulting mixture was adjusted by adding THF to make a solid content of 20%. It was then cast on a glass plate and cured at different temperatures for the desired times. The plate was immersed in boiling water for 30 min, and then the transparent sheet of PU–NKGM was peeled off the glass plate. The thickness of the sheet was measured to be about  $100 \mu\text{m}$ . By altering the content of NKGM in the sheets to 10, 20, 30, 40, and 50 wt %, a series of sheets coded as PUNK-1, PUNK-2, PUNK-3, PUNK-4m and PUNK-5 was prepared. The pure PU sheet was coded as PU-0. The sheets were vacuum-dried at room temperature for 3 days, and then were used for the measurements.

### Apparatus and Characterization

The surface and cross-section morphology of the sheets were observed using a scanning electron microscope (SEM; Hitachi S-570, Japan). The samples were successively frozen in liquid nitrogen, snapped, vacuum-dried, and coated with gold before observation. IR spectra of the samples were recorded with a Nicolet 170SX Fourier



**Figure 1** FTIR spectra of konjac glucomannan (KGM) and nitrokonjac glucomannan (NKGM).



**Figure 2** SEM photographs of the sheets (all photographs are surfaces of the sheets except for PU-0-B).

transform IR (FTIR) spectrometer. The sheets were cut into 1-mm squares and then blended with potassium bromide in order to laminate. The light transmittance of the sheets was measured with a UV-vis spectrophotometer (Shimadzu UV-160, Japan) over wavelengths from 400 nm to 800 nm, and sheet thickness was 100  $\mu\text{m}$ . The tensile strength ( $\sigma_b$ ) and breaking elongation ( $\epsilon_b$ ) of the sheets were tested on a tensile tester (CMT-6503, Shenzhen SANS Test Machine Co. Ltd., China) with rate of 100 mm/min. The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) of the sheets were performed using a thermoanalyzer (DT-40, Shimadzu Co., Japan) under a nitrogen atmosphere at a flow rate of 30 mL/min and at a heating rate of 10°C/min. The temperature region covered by the DTA was 0–500°C, and that of TGA was 0–600°C.

## RESULTS AND DISCUSSION

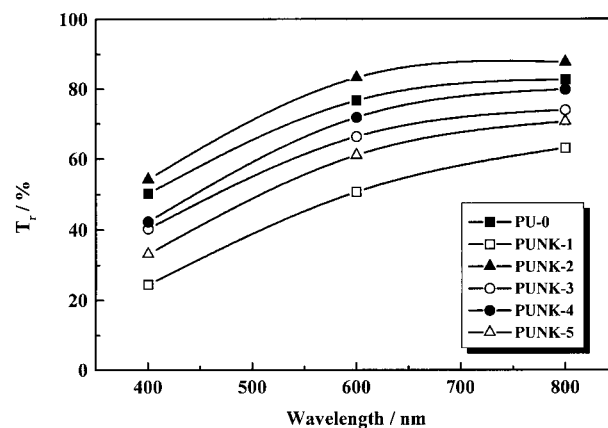
### Structure and Miscibility

The SEM micrographs of the sheets are shown in Figure 2. The surface [Fig. 2(a)] of the pure PU

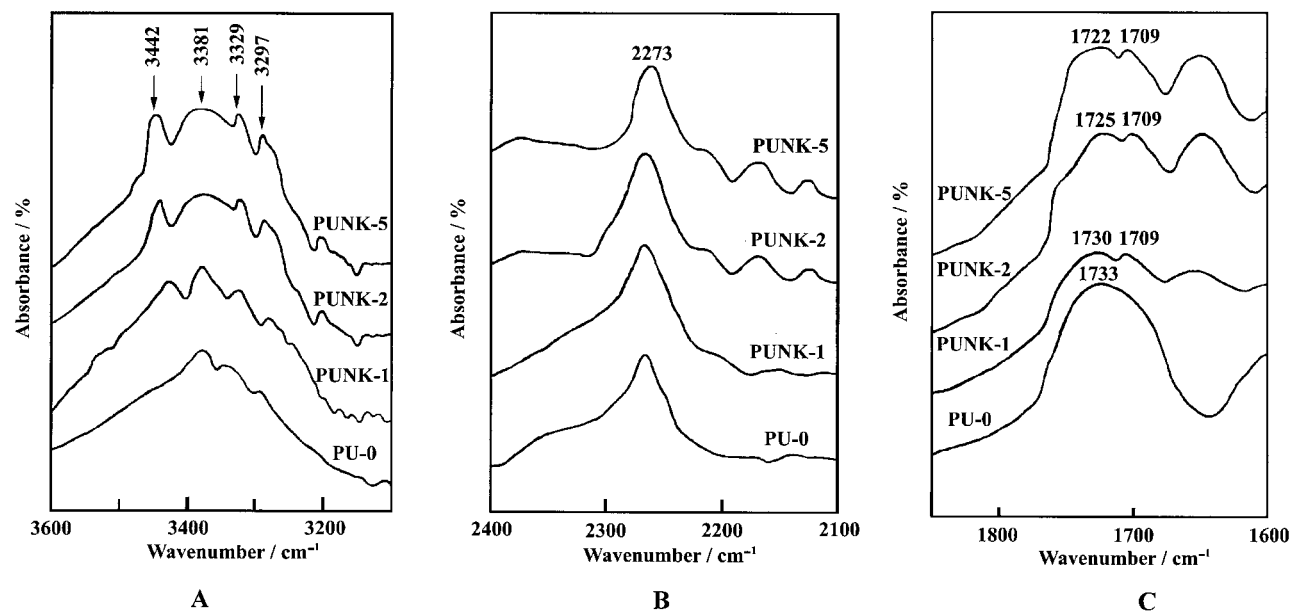
sheet showed heterogeneous morphology, but its cross section [Fig. 2(b)] was homogeneous. The surface of the pure NKGM sheet showed a dense microporous structure, and this loose structure was related to the brittleness of the NKGM sheet. Usually, a SEM micrograph is used to identify the blend miscibility of two polymers based on homogeneous surface and cross section. It can obviously be seen that the PUNK-4 sheet had a surface with a homogeneous and compact structure, showing miscibility between the two components. It can be assumed that this was the consequence of a strong interaction occurring, caused by the interpenetrating of NKGM and PU. With the increase of the content of NKGM to 50 wt %, the PUNK-5 sheet showed a porous surface, denoting that phase separation has occurred.

The percent light transmittances ( $T$ ) of the sheets measured at different wavelengths are shown in Figure 3. The transparency of the material is an auxiliary criterion to judge the miscibility of blend films.<sup>26</sup> It is obvious that the light transmittances increased with the increase of wavelength from 500 to 800 nm. It is worth noting that the PUNK-2 sheet showed a higher light transmittance than did PU-0, suggesting the good miscibility and strong interchains interaction between the nitrokonjac glucomannan and PU networks.

FTIR spectroscopy is a useful tool for the characterization of hydrogen bonding in polyurethanes.<sup>27</sup> Figure 4 shows the FTIR spectra of the sheets over the wavelength region of 1600–3600. Figure 4(a) shows that a new stretching band of N—H around 3442  $\text{cm}^{-1}$ , which is absent from the PU-0 sheet, and is assigned to the free N—H



**Figure 3** Percent light transmittance ( $T_r$ ) of the sheets measured at different wavelengths.



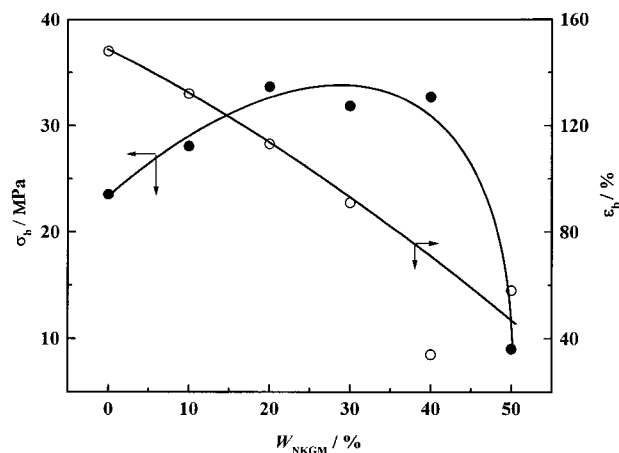
**Figure 4** FTIR spectra of the sheets in the wavelength region of (a) 3600–3100  $\text{cm}^{-1}$ , (b) 2400–2100  $\text{cm}^{-1}$ , and (c) 1850–1600  $\text{cm}^{-1}$ .

groups,<sup>28</sup> appeared in the spectra of the PUNK-1, PUNK-2, and PUNK-5 sheets. This change indicates that the original hydrogen bonding in the PU-0 sheet was interrupted because of the introduction of NKG. The two bands at 3381  $\text{cm}^{-1}$  and 3297  $\text{cm}^{-1}$  for PUNK sheets are assigned to the carbonyl vibrations in Fermi resonance with the N—H stretching fundamental vibration.<sup>29</sup> The peak at 3381  $\text{cm}^{-1}$  broadened, compared with the PU sheet. Furthermore, the shoulder peak of hydrogen-bonded N—H at 3329  $\text{cm}^{-1}$ <sup>29</sup> for PUNK sheets became more intense than that for PU. These data indicate that new intermolecular hydrogen bonding between the NKG and PU occurred in the PUNK sheets. Figure 4(b) shows the —NCO bands appeared at 2273  $\text{cm}^{-1}$  in the PU and that the PUNK sheets almost did not change, suggesting no occurrence of chemical bonds between NKG and PU—that is, the excessive —NCO groups of PU were still retained in the PUNK sheets. Interestingly, a new stretching band at 1709  $\text{cm}^{-1}$ , assigned to the hydrogen-bonded urethane carbonyl groups,<sup>30</sup> appeared in the IR spectra of the PUNK-1, PUNK-2, and PUNK-5 sheets, indicating that the hydrogen bonding was caused by the introduction of NKG. The IR results suggest that the interpenetration and entanglement between NKG and PU exist in the PUNK sheets, resulting in a semi-IPN structure, in which the linear molecules of NKG interpenetrated into the PU networks.

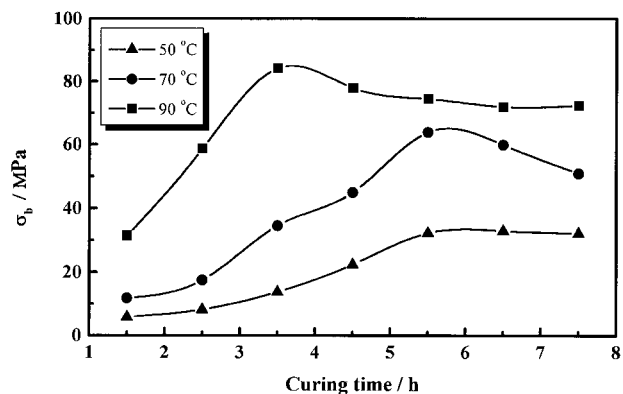
The intermolecular interaction can be attributed to hydrogen bonding between the —ONO<sub>2</sub> groups in NKG and NH—C=O groups in PU. The NKG molecules play an important role in the formation of the interpenetrating networks.

#### Effect of NKG on Mechanical Properties

The tensile strength ( $\sigma_b$ ) and breaking elongation ( $\epsilon_b$ ) of the sheets as a function of the NKG content ( $W_{\text{NKG}}$ ) are shown in Figure 5. At first the  $\sigma_b$  increased with an increase of the  $W_{\text{NKG}}$ ;



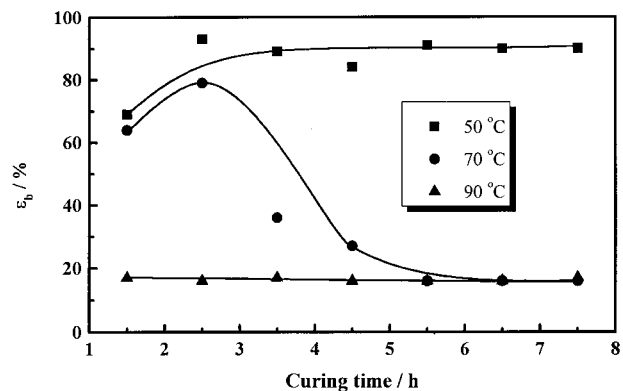
**Figure 5** Effects of nitrokonjac glucomannan ( $W_{\text{NKG}}$ ) content on tensile strength ( $\sigma_b$ ) and breaking elongation ( $\epsilon_b$ ) of sheets cured at 50°C.



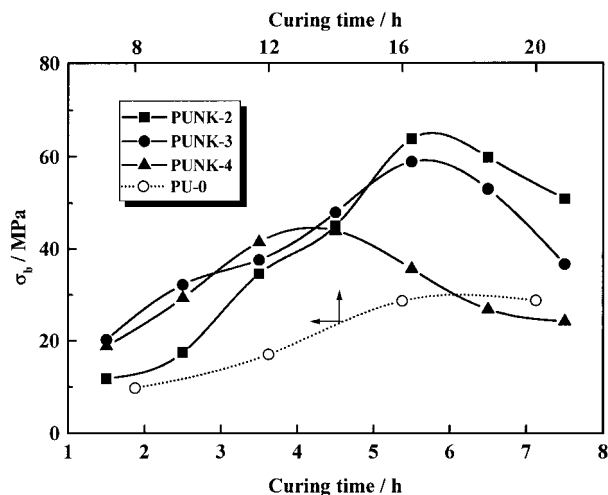
**Figure 6** Effects of curing time on tensile strength ( $\sigma_b$ ) of PUNK-2 sheet cured at different temperatures.

then it sharply decreased as the  $W_{\text{NKGM}}$  exceeded 40 wt %. The  $\epsilon_b$  decreased with the increase of  $W_{\text{NKGM}}$ . This can be explained by the rigidity of NKGM chains being greater than that of PU, so that the embedding of NKGM into the PU network restricted the movement of the chain segments, resulting in a decrease in the flexibility of PU.

Figures 6 and 7 show the effects of curing time on the  $\sigma_b$  and  $\epsilon_b$  of the PUNK-2 sheet. The  $\sigma_b$  value of the sheet cured at a relatively high temperature more quickly reached the maximum  $\sigma_b$  than that cured at relatively low temperature. However, the  $\epsilon_b$  value of the PUNK sheets cured at 70 °C and 90 °C decreased significantly. When the curing temperature was 90 °C or the curing time exceeded about 6 h at 70 °C, the  $\epsilon_b$  value decreased. This can be explained by the bonded water in NKGM being removed at a relatively longer curing time or a high curing temperature,



**Figure 7** Effects of curing time on breaking elongation ( $\epsilon_b$ ) of PUNK-2 sheet cured at different temperatures.



**Figure 8** Effects of curing time on tensile strength ( $\sigma_b$ ) of sheets cured at 70 °C.

thus making the PUNK sheets become brittle. Compared with the data in Figure 5, the  $\sigma_b$  (32 MPa) and  $\epsilon_b$  (93%) of PUNK-3 sheet hardly changed after immersing in water for 24 h, showing the good water resistance of the PUNK sheets. In view of the data, optimum curing time and temperature used in this work were 5–6 h and 50 °C, respectively.

The effects of the curing time on the  $\sigma_b$  of the sheets cured at 70 °C are shown in Figure 8. Under the same experimental condition, the curing time for the PUNK-2, PUNK-3, and PUNK-4 sheets was 5 h, but that for the PU-0 sheet was more than 16 h. Moreover, the  $\sigma_b$  of the PUNK sheets was obviously higher than that of the PU sheet. Importantly, the addition of NKGM significantly shortened the curing time. The curing time of the PUNK sheets decreased with an increase of NKGM. Therefore, the NKGM plays an important role in accelerating the cure for the PUNK sheets.

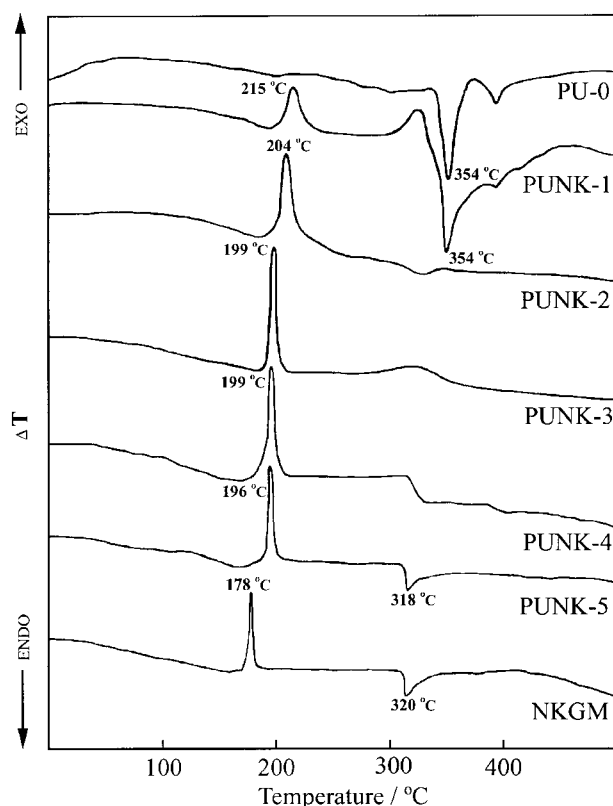
### Effect of NKGM on Thermal Properties

The DTA thermograms of the sheets are shown in Figure 9. The endothermic peak at 354 °C, corresponding to the decomposition of the PU network, disappeared with the increase of NKGM to 20 wt % in the PUNK sheets. However, the endothermic peak at 320 °C assigned to the disintegrated temperature of NKGM<sup>31</sup> shifted to 318 °C for the PUNK-5 sheet. A sharp exothermic peak caused by NKGM in the thermogram of the PUNK sheets shifted from 196 °C to 215 °C with the decrease of

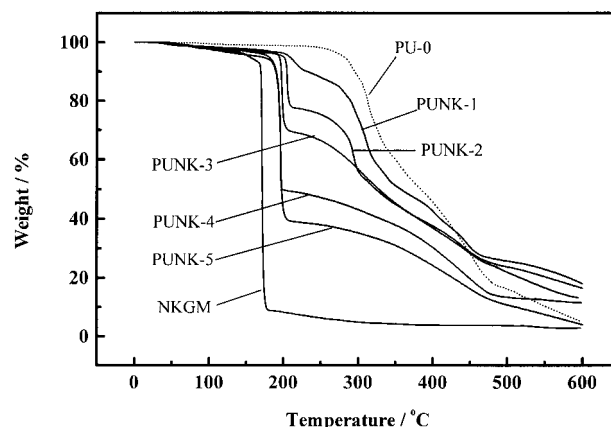
NKGM in the PUNK sheets. These results are in good agreement with the maximum weight loss of the sheets, shown in the TGA thermograms (Fig. 10). The temperatures corresponding to the weight loss transition are 215°C, 205°C, 198°C, 196°C, and 196°C for the PUNK-1, PUNK-2, PUNK-3, PUNK-4, and PUNK-5 sheets, respectively. That is, the thermal stability decreased with the increase of NKGM. However, the residue at 600°C of PUNK-2, PUNK-3, and PUNK-4 sheets (20%, 18%, and 13%, respectively) was higher than that of PU (10%), suggesting a strong intermolecular interaction between NKGM and PU caused by hydrogen bonding, which hindered the thermal decomposition of the PUNK sheets.<sup>15,32</sup>

## CONCLUSIONS

A water-insoluble nitrokonjac glucomannan (NKGM) was successfully synthesized by reacting konjac glucomannan with fuming nitric acid containing sulfuric acid and P<sub>2</sub>O<sub>5</sub> at 20°C. Semi-interpenetrating polymer network sheets each about 100



**Figure 9** DTA thermograms of sheets of PU, PUNK, and NKGM.



**Figure 10** TGA thermograms of sheets of PU, PUNK, and NKGM.

μm thick were prepared at 50°C for 5–6 h from 10%–40% NKGM with castor oil-based polyurethane (PU). Hydrogen bonding between NKGM and PU exists in the semi-IPNs sheets, resulting in their miscibility. When the NKGM content in the PUNK sheets was 20 wt %, the mechanical properties, thermostability, and light transmittance were significantly higher than for the PU sheet. The NKGM in the PUNK sheets plays an important role in enhancing the tensile strength and in accelerating the cure. This new material, containing 20–40% nitrokonjac glucomannan, not only has a performance similar to PU, but it also has benefits for environmental protection because of its biodegradability.

## REFERENCES

1. Coleman, M. M.; Zarian, J. J. *Polym Sci, Polym Phys Ed* 1979, 17, 837.
2. Thomas, D. A.; Sperling, L. H. *Polymer Blends*; Plenum: New York, 1979; Vol. II.
3. Sperling L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981.
4. Huelck, V.; Thomas, D. A.; Sperling, L. H. *Macromolecules* 1972, 5(4), 340.
5. Widmaier, J. M.; Sperling, L. H. *Br Polym J* 1984, 16, 46.
6. Kim, S. C.; Klempner, D.; Frisch, K. C.; Radigan, W.; Frisch, H. L. *Macromolecules* 1976, 9(2), 258.
7. Kim, S. C.; Klempner, D.; Frisch, K. C.; Frisch, H. L. *Macromolecules* 1977, 10(6), 1187.
8. Hourston, D. J.; Schäfer, F. U. *J Appl Polym Sci* 1996, 62, 2025.

9. Hourston, D. J.; Zia, Y. *J Appl Polym Sci* 1984, 29, 2951.
10. Barrett, L. W.; Ferguson, G. S.; Sperling, L. H. *J Polym Sci, Part A: Polym Chem* 1993, 31, 1287.
11. Patel, P.; Shah, T.; Suthar, B. *J Appl Polym Sci* 1990, 40, 1037.
12. Devia, N.; Manson, J. A.; Sperling, L. H. *Macromolecules* 1979, 12(3), 360.
13. Raymond, M. P.; Bui, V. T. *J Appl Polym Sci* 1998, 70, 1649.
14. Nishio, Y.; Koide, T.; Miyashita, Y.; Kimura, N. *J Polym Sci, Part B: Polym Phys* 1999, 37, 1533.
15. Zhang, L.; Zhou, Q. *J Polym Sci, Part B: Polym Phys* 1999, 37, 1623.
16. Gong, P.; Zhang, L. *Ind Eng Chem Res* 1998, 37, 2681.
17. Gong, P.; Zhang, L.; Zhuang, L.; Lu, J. *J Appl Polym Sci* 1998, 68, 1321.
18. Zhang, L.; Zhou, Q. *Ind Eng Chem Res* 1997, 36, 2651.
19. Zhang, L.; Zhou, J.; Huang, J.; Gong, P.; Zhou, Q.; Zheng, L.; Du, Y. *Ind Eng Chem Res* 1999, 38, 4284.
20. Kato, K.; Matsuda, K. *Agric Biol Chem* 1972, 36(4), 639.
21. Millane, R. P.; Hendrixson, T. L. *Carbohydr Polym* 1994, 25, 245.
22. Jia, C.; Chen, S.; Mo, W.; Meng, Y.; Yang, L. *Chinese Biochemical J* 1988, 4(5), 407.
23. Hourston, D. J.; Zia, Y. *J Appl Polym Sci* 1984, 29, 2963.
24. Kishida, N.; Okimasu, S.; Kamata, T. *Agric Biol Chem* 1978, 42(9), 1645.
25. Williams, D. H.; Fleming, I. *Spectroscopic Methods on Organic Chemistry*, 3rd ed.; McGraw-Hill: London, 1980; p. 44.
26. Krause, S. *J Macromol Sci: Rev Macromol Chem C* 1972, 7, 251.
27. Koberstein, J. T.; Gancarz, I. *J Polym Sci, Part B: Polym Phys* 1986, 24, 1401.
28. Teo, L. S.; Chen, C. Y.; Kuo, J. F. *Macromolecules* 1997, 30, 1793.
29. Coleman, M. M.; Lee, K. H.; Skrovanek, D. J.; Painter, P. C. *Macromolecules* 1986, 19, 2149.
30. Luo, N.; Wang, D. N.; Sheng, S. K. *Polymer* 1996, 37(14), 3045.
31. Xiao, C.; Gao, S.; Wang, H.; Zhang, L. *J Appl Polym Sci* 2000, 76, 509.
32. Aly, K. I. *Polymer Int* 1999, 48, 773.