

# Synthesis and Characterization of Poly(ester urethane)/Nitrokonjac Glucomannan Semi-Interpenetrating Polymer Networks

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**ABSTRACT:** We prepared novel semi-interpenetrating polymer network (semi-IPN) materials by mixing poly(ester urethane), synthesized by the polymerization reaction between poly(ethylene glycol adipate) and toluene diisocyanate in the presence of 2,2-bis(hydroxyl methyl) propionic acid as an extender, with nitrokonjac glucomannan (NKGM) in tetrahydrofuran and then by crosslinking and curing the mixture at 60°C for 1.5 h. Miscibility and the properties of the sheets were studied by Fourier transition infrared spectroscopy, wide-angle X-ray diffraction, differential scanning calorimetry (DSC), and scanning electron microscopy. The results indicate that strong interactions between poly(ester urethane) and NKGM in the semi-IPN sheets occurred, lead-

ing to good miscibility between the two polymers in the whole region of component ratios. When the content of NKGM was 10%, the tensile strength and breaking elongation of the semi-IPN sheet were simultaneously enhanced to 35 MPa and 960%, respectively, compared with pure polyurethane. The DSC curves showed a low softening temperature for the poly(ester urethane), which resulted in the high elongation. By changing the NKGM amount from 10 to 90%, we prepared a series of composite materials from an elastomer to tough plastics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2224–2228, 2003

**Key words:** elastomers; Konjac glucomannan; polyurethane

## INTRODUCTION

Interpenetrating polymer networks (IPNs) prepared from polyurethane (PU) and other polymers, such as unsaturated polyester and epoxy resin, are an important focus in composite material domain.<sup>1</sup> IPN systems always show complicated relaxation behavior because of their structural complexity.<sup>2</sup> According to the different types of polyols used to react with isocyanates, the resulting PUs can be divided into poly(ester urethane) and poly(ether urethane). In general, the former has better biodegradability than the latter.<sup>3,4</sup> Polysaccharides with hydroxyl groups per repeating units, such as lignin and its derivatives, can theoretically be used as polyols to react with isocyanates to prepare PUs.<sup>5,6</sup> Recently, semi-interpenetrating polymer network (semi-IPN) materials from castor-oil-based PU and other natural polymers, such as chitosan,<sup>7</sup> nitrochitosan,<sup>8</sup> nitrocellulose,<sup>9</sup> and benzoyl konjac glucomannan,<sup>10</sup> have been synthesized and studied. The interpenetration and entanglement of natural polymers into PU networks occurs during

mixing and curing, resulting in intimate interactions between the two polymers. As a result, novel biodegradable composite materials with improved mechanical properties can be obtained.

In our latest study, we prepared a series of semi-IPNs by mixing a castor-oil-based PU prepolymer and linear nitrokonjac glucomannan (NKGM) in tetrahydrofuran (THF) and curing the mixture at 50°C in the presence of a chain extender and a crosslinking agent.<sup>11</sup> NKGM with a relatively low weight-average molecular weight ( $M_w \leq 8.44 \times 10^4$ ) is beneficial for the enhancement of the miscibility between PU and NKGM and can significantly improve the mechanical properties and optical transmittance (Tr) of semi-IPN materials.<sup>12</sup> In this study, we synthesized semi-IPNs from poly(ester urethane) and NKGM and examined the structure and properties of this material. By comparing the results of this study with our previous one, we elucidated the difference between these two kinds of semi-IPN materials.

## EXPERIMENTAL

### Synthesis of NKGM

Konjac glucomannan, a natural polysaccharide composed of  $\beta$ -1,4-pyranosid-backbone-linked  $\beta$ -D-mannose and  $\beta$ -D-glucose in the approximate ratio 1.6:1, was isolated and purified from tubers of *Amorphophallus konjac* according to the previous method.<sup>13</sup> The

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synthesis of NKGM was reported in another article, and its average degree of substitution and  $M_w$  were 2.4 and  $4.75 \times 10^4$ , respectively.<sup>11</sup>

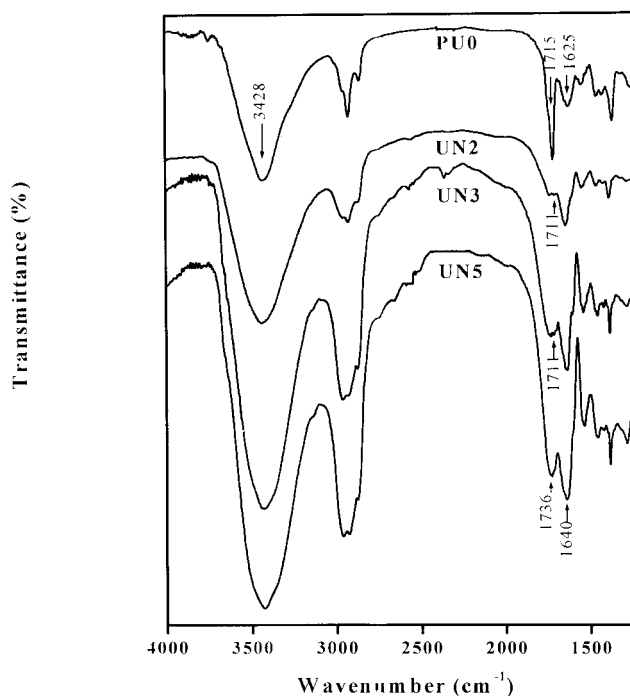
### Synthesis of PU/NKGM semi-IPNs

The value of  $[\text{NCO}]/[\text{OH}]$  was predetermined theoretically to be 1. A three-necked flask was fitted with a nitrogen inlet tube, a stirrer, and a pressure-equalizing dropping funnel. Poly(ethylene glycol adipate) (66.5 g;  $M_w = 2150$ ; Zhangting Polyurethane Factory, Sichuan, China; vacuum-dried for 5 h at 110°C before use) was added into the flask and was heated to 120°C to produce a poly(ethylene glycol adipate) melt. Toluene diisocyanate (11.6 g; redistilled under reduced pressure to dehydrate it before use) was dropped into the flask through the dropping funnel for 10 min under a nitrogen atmosphere. We controlled the polymerization reaction at 80°C for 2 h to obtain the PU prepolymer. Then, we poured 3.5 g of 2,2-bis(hydroxyl methyl) propionic acid (Chengdu Polyurethane Factory, Chengdu, China; vacuum-dried for 5 h at 110°C before use) into the flask to continue the chain-extending reaction for 1 h. After the mixture was cooled to 40°C, 90 g of THF was added. The solid content of the resulting mixture was diluted to 48 wt % by mechanical mixing.

This mixture (6 g), a predetermined amount of NKGM, and 0.1 g of diethylene triamine (Third Chemical Reagent Factory of Yixing, Jiangu, China) were mechanically mixed in THF in a flask for 3 h. We adjusted the contents of the mixture to 15 wt % by controlling the amount of THF. The mixture was cast on a glass plate and cured at 60°C for 1.5 h, then the plate with product was immersed in boiling water for 10 min, and finally, the transparent sheet was peeled off. The thickness of the sheet was measured to be about 100  $\mu\text{m}$ . By altering the percentage content of NKGM ( $w_{\text{NKGM}}$ ) in the sheets to 10, 20, 30, 40, 50, 70, and 90 wt %, we prepared a series of sheets coded as UN1, UN2, UN3, UN4, UN5, UN6, and UN7. The pure PU sheet was coded as PU0, and the sheet from pure NKGM could not be obtained by the casting method because of its brittleness. The sheets were vacuum-dried at room temperature for 3 days and were then used for the measurements.

### Apparatus and characterization

IR spectra of the samples were recorded with a Nicolet 170SX Fourier transform infrared (FTIR) spectrometer (Minnesota). We cut the sheets to 1 mm in length and 1 mm in width and then mixed them with potassium bromide to make a molded sheet. The surface and cross-section morphology of the sheets were observed with a scanning electron microscope (Hitachi S-570, Tokyo, Japan). The samples were frozen in liquid ni-



**Figure 1** FTIR spectra of the UN2, UN3, UN5, and PU0 sheets.

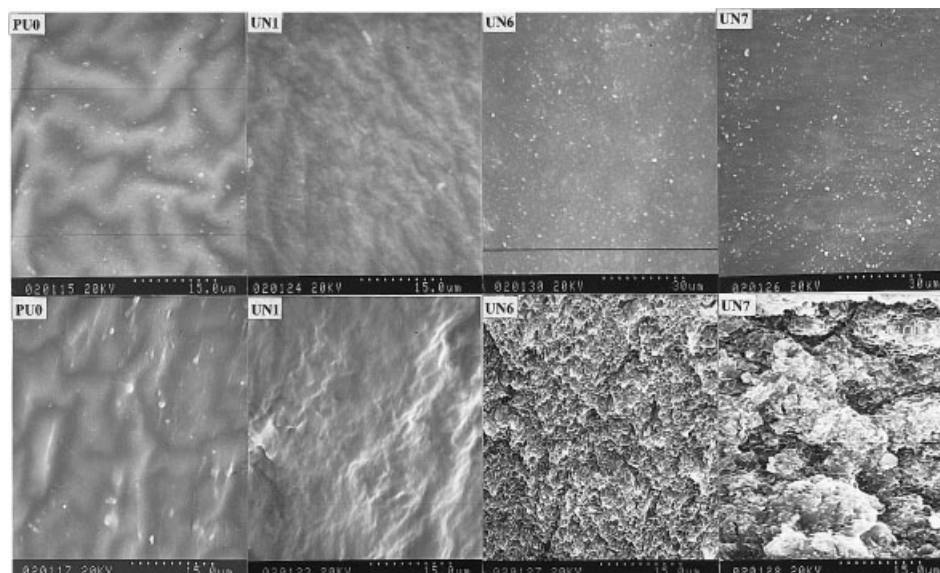
trogen, snapped, vacuum-dried, and coated with gold before observation. Wide-angle X-ray diffraction (WAXRD) patterns of the sheets were recorded on an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Tokyo, Japan) with Cu  $K\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) at 40 kV and 30 mA with a scanning rate of  $10^\circ/\text{min}$ . The diffraction angle ( $2\theta$ ) ranged from 5 to  $40^\circ$ . Differential scanning calorimetry (DSC) tests of the samples were performed with a DSC-2 C thermal analyzer (PerkinElmer Co., Boston, MA) under a nitrogen atmosphere (30 mL/min) at a heating rate of  $10^\circ\text{C}/\text{min}$  from  $-60$  to  $150^\circ\text{C}$ .

The Tr of the sheets was measured with an ultraviolet–visible spectrophotometer (Shimadzu UV-160, Kyoto, Japan) over wavelengths from 400 to 800 nm, and the thickness of the sheets used 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., Shenzhen, China) with a tensile rate of 100 mm/min according to ISO 6239-1986.

## RESULTS AND DISCUSSIONS

### Structure and miscibility

Figure 1 shows the FTIR spectra of the UN2, UN3, UN5, and PU0 sheets at the wavenumber region of  $4000\text{--}1200 \text{ cm}^{-1}$ . The intensity of the absorption band around  $3428 \text{ cm}^{-1}$ , assigned to the stretching of secondary amino groups, became obviously stronger

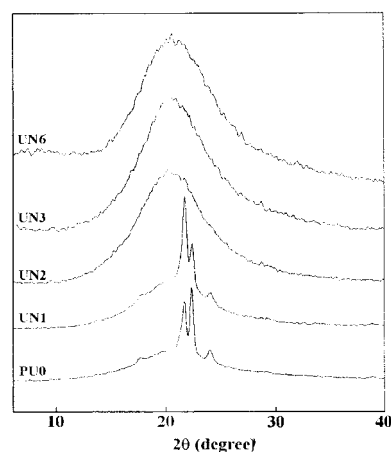


**Figure 2** SEM photographs of the (top) free surface and (bottom) cross-section for the sheets.

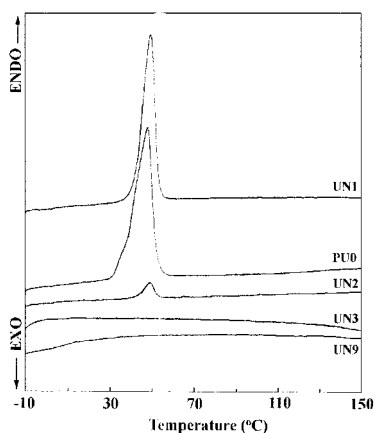
than that of PU0, suggesting the occurrence of intermolecular interactions between PU and NKGM. The absorption band at  $2960\text{ cm}^{-1}$ , assigned to the stretching of methylene groups of the PU soft segment, became gradually stronger with increasing  $w_{\text{NKGM}}$ . The absorption band at  $1715\text{ cm}^{-1}$ , assigned to the hydrogen-bonded carbonyl of urethane groups<sup>14</sup> in PU0, shifted to  $1711\text{ cm}^{-1}$  for the UN composite sheets. Simultaneously, the typical absorption band of the amide I of urethane groups shifted from  $1625\text{ cm}^{-1}$  for PU0 to  $1640\text{ cm}^{-1}$  for the composite sheets, similar to the semi-IPN sheets.<sup>15</sup> These results confirm the formation of new hydrogen bonding in the composite system, which mainly resulted from the interaction between the urethane groups of PU and the  $-\text{ONO}_2$  groups of NKGM. This phenomenon also appeared in the semi-IPN system prepared from castor-oil-based PU and NKGM, as explained before.<sup>11</sup> Therefore, the UN composite sheets also had a semi-IPN structure.

Figure 2 shows the scanning electron microscopy (SEM) photographs of the surface and cross-section of the PU0 and UN sheets. When  $w_{\text{NKGM}}$  in the composite sheet was 10%, the surface and cross-section morphologies of the sheet UN1 were homogeneous and compact, suggesting a good miscibility. When  $w_{\text{NKGM}}$  was higher than 30%, microphase separation appeared. Only small particles appeared on the surface of the semi-IPN sheets, including UN6 and UN7, and no obvious phase separation appeared on the cross-section when  $w_{\text{NKGM}}$  was increased from 10 to 90%, which suggests that the two polymers had good or some degree of miscibility in the whole region of component ratios. This could be attributed to the strong interaction between poly(ester urethane) and NKGM in the semi-IPN system.

Figure 3 shows the WXR D patterns of the UN1, UN2, UN3, and UN6 composite sheets. The three crystal peaks at  $2\theta$  values of  $20.6$ ,  $21.1$ , and  $22.3^\circ$  for PU0 sheets could be attributed to the order arrangement of PU soft segments.<sup>16</sup> When 10% NKGM was added, the intensity of the crystal peaks at  $20.6$  and  $22.3^\circ$  became weaker. This suggests that the arrangement of soft and hard segments of PU was perturbed by the addition of NKGM. The crystallinities of the PU0 and UN1 sheets were 43 and 40%, respectively. Only a wide diffraction peak appeared for each semi-IPN sheet when the  $w_{\text{NKGM}}$  reached 20%, suggesting the amorphous nature of the sheets. Generally, when the crystalline component and the noncrystalline component in a composite material are good miscible, its crystallinity is lower than the individual crystalline component. It



**Figure 3** WXR D diffraction patterns of the UN1, UN2, UN3, UN6, and PU0 sheets.



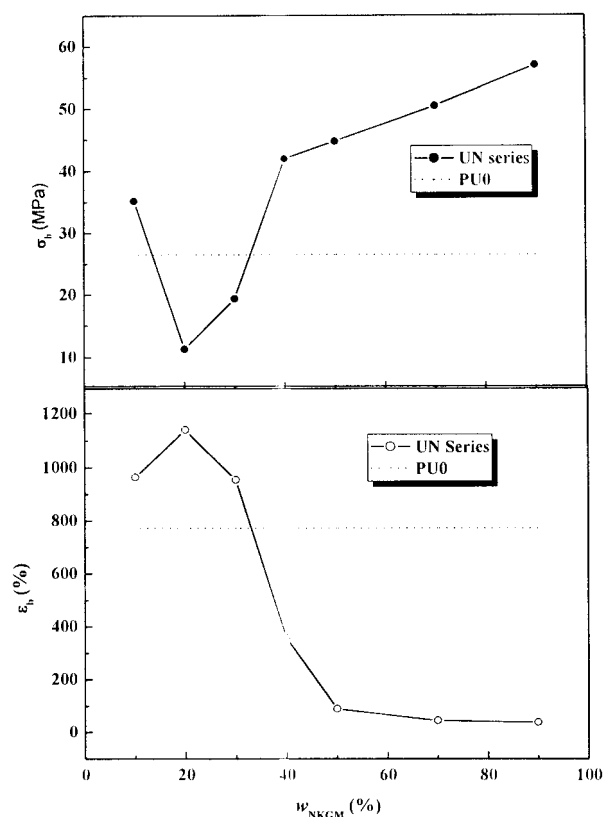
**Figure 4** DSC thermograms of the UN1, UN2, UN3, UN9, and PU0 sheets.

this case, the change in crystallinity was attributed to the strong interaction between PU and NKGM.

Figure 4 shows the DSC curves of the UN1, UN2, UN3, UN9, and PU0 sheets. The temperature of melting transition ( $T_m$ ), namely, the softening temperature for the network structure, appeared at 36.0, 41.8, and 42.9°C for the PU0, UN1, and UN2 sheets, respectively. The low softening temperature of the sheets reflected the easy mobility of the PU molecules. However, the elevation of  $T_m$  of the UN sheets in contrast to the PU0 sheets indicated that the molecular motion of PU in the UN was limited by the addition of NKGM because of the interaction between the two polymers. When  $w_{\text{NKGM}}$  was higher than 30%, the  $T_m$  disappeared, suggesting that the intermolecular interaction became greater, resulting in the complete inhibition of the molecular motion of PU. This result supports the conclusion of miscibility between PU and NKGM in the UN sheets and was in good agreement with those from SEM and WXR. D.

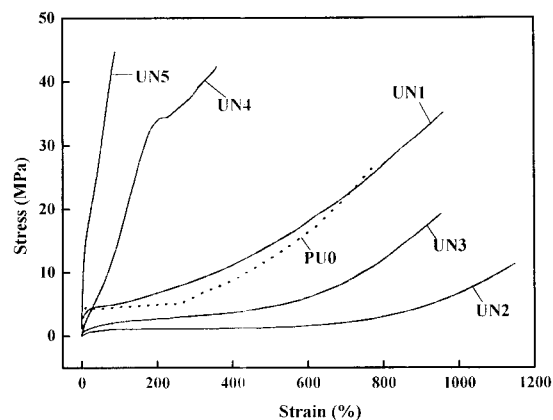
### Properties of semi-IPNs

Figure 5 shows the effect of  $w_{\text{NKGM}}$  on  $\sigma_b$  and  $\epsilon_b$  of the composite sheets.  $\sigma_b$  of the UN sheets was higher than that of PU0 when  $w_{\text{NKGM}}$  was 10%. However, when  $w_{\text{NKGM}}$  was more than 10%,  $\sigma_b$  of the sheets UN decreased until 30% NKGM. Interestingly, when  $w_{\text{NKGM}}$  was higher than 40%,  $\sigma_b$  of the composite sheet was higher than that of PU0.  $\epsilon_b$  of the UN1, UN2, and UN3 sheets was higher than that of PU0, suggesting that the addition of NKGM from 10 to 30% improved the toughness of the composite materials. The toughness-reinforcement and strength-reinforcement effects of a small amount of nitro lignin on PU was also found in a previous work,<sup>17</sup> in which 2.8% nitro lignin in graft IPN materials played an important role in the simultaneous enhancement of  $\sigma_b$  and  $\epsilon_b$  because of the formation of a relatively large network. Interestingly,  $\sigma_b$

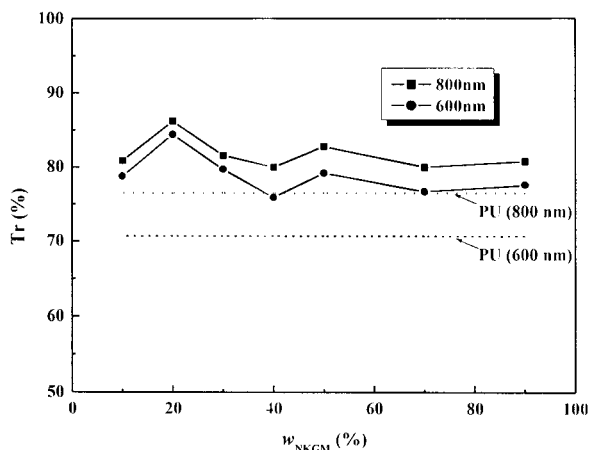


**Figure 5** Dependence of the sheets'  $\sigma_b$  and  $\epsilon_b$  values on  $w_{\text{NKGM}}$ .

and  $\epsilon_b$  of the UN1 sheet were simultaneously improved compared to PU0. We interpreted that the addition of 10% NKGM not only resulted in strong interactions between PU and NKGM but also kept the PU networks. Also, the addition of NKGM resulted in the microphase separation between the soft and hard segment of PU; as a result,  $\epsilon_b$  also increased. Thus, both  $\sigma_b$  and  $\epsilon_b$  of the UN1 sheet were enhanced. When the  $w_{\text{NKGM}}$  reached 40%,  $\sigma_b$  of the UN sheets increased with increasing  $w_{\text{NKGM}}$ , but  $\epsilon_b$  sharply decreased.



**Figure 6** Tensile stress-strain curves of the UN1, UN2, UN3, UN4, UN5, and PU0 sheets.



**Figure 7** Dependence of the sheets Tr values on  $w_{\text{NKGM}}$  at wavelengths of 600 and 800 nm.

Figure 6 shows the tensile stress–strain curves for the UN1, UN2, UN3, UN4, UN5, and PU0 sheets at room temperature. When  $w_{\text{NKGM}}$  was 10–30%, the composite material exhibited the flexibility of rubber. When  $w_{\text{NKGM}}$  reached 40%, the slope of the initial linear part of the curve increased. Namely, the stress sharply increased, whereas the strain only had a minor increase corresponding to the tensile behavior of a tough material. Generally, the area under the stress–strain curves reflects the toughness of the materials.<sup>18</sup> As shown in Figure 6, the area under the curve of the UN1 sheet was obviously greater than that of the other semi-IPN sheets and PU0, suggesting good flexibility and toughness.  $\epsilon_b$  and  $\sigma_b$  of the UN1 sheet reached 960% and 35 MPa, respectively. The high flexibility and elongation were correlated with the low softening temperature of the poly(ester urethane) component. The UN1–UN3 sheets could be used as elastic materials. Therefore, by adjusting  $w_{\text{NKGM}}$ , we obtained a series of novel materials from elastomer to plastic.

Figure 7 shows the Tr of the semi-IPN sheets and PU0 at wavelengths of 600 and 800 nm. Interestingly, the Tr values of all of the semi-IPN sheets were higher than that of PU0. Tr of the semi-IPN sheets was above 80%, a relatively high Tr. As confirmed by the results of FTIR, WXR, and DSC, NKGM intimately entangled and interacted with PU, resulting in good miscibility. These novel materials (the UN series) possessed

biodegradability, a high Tr, and good mechanical properties.

## CONCLUSIONS

We prepared a series of semi-IPN sheets by mixing poly(ester urethane) and NKGM in THF and then by crosslinking and curing the mixture. When  $w_{\text{NKGM}}$  ranged from 10 to 90%, the semi-IPN sheets showed good miscibility or some degree of miscibility. The good Tr of the semi-IPN sheets indicated that the strong interaction between PU and NKGM resulted from the interpenetration and entanglement of NKGM into the PU network. When  $w_{\text{NKGM}}$  was 10%, the semi-IPN sheets possessed the highest elongation, flexibility, and Tr and could be used as good elastic materials. When  $w_{\text{NKGM}}$  exceeded 40%, the semi-IPN sheets showed a high  $\sigma_b$  and hardness and could be used as tough plastics.

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