

# Effect of the Synthesis Route on the Structure and Properties of Polyurethane/Nitrokonjac Glucomannan Semi-Interpenetrating Polymer Networks

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**ABSTRACT:** With a synthesis route differing from previous methods, novel semi-interpenetrating polymer networks (semi-IPNs), coded UNK-II, were synthesized by the initial mixing of nitrokonjac glucomannan (NKGM) with castor oil in butanone and the subsequent addition of toluene diisocyanate (TDI) to begin the polymerization reaction in the presence of 1,4-butanediol (BD) as a chain extender at 60°C. The results from dynamic mechanical analysis, differential scanning calorimetry, and ultraviolet spectroscopy indicated that a certain degree of microphase separation occurred between soft and hard segments of polyurethane (PU) in the UNK-II sheets. The  $\alpha$ -transition temperature, glass-transition temperature, heating capacity, and tensile strength increased with an increase in the NKGM content, and this suggested an interaction between PU and NKGM in the UNK-II sheets. In a previous method, semi-IPN materi-

als (PUNK) were synthesized by the polymerization reaction between castor oil and TDI, and then this PU prepolymer was mixed with NKGM and cured in the presence of BD as a chain extender. The PUNK sheets had relatively good miscibility and mechanical properties. However, for UNK-II sheets prepared by the method reported in this work, NKGM mainly played a role in reinforcement. When the NKGM content was less than 10%, the UNK-II sheets exhibited good miscibility, tensile strength (26–28 MPa), and breaking elongation (130–140%), similar to those of PUNK materials. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1948–1954, 2003

**Key words:** polyurethanes; interpenetrating networks (IPN); biodegradable

## INTRODUCTION

The chemical exploitation of renewable resources, such as plant biomass, constitutes a promising and indeed auspicious alternative to the use of nonrenewable fossil resources and represents a rich and varied source of polymers.<sup>1</sup> Therefore, the preparation of polymers from renewable resources has attracted considerable attention from polymer scientists throughout the world because of their potential as substitutes for petrochemical derivatives.<sup>2</sup> Making use of natural polymers not only protects the environment from pollution but also saves limited oil resources. Biodegradable polymers can be prepared by the chemical or physical combinations of synthetic polymers and natural polymers.<sup>3</sup> Interpenetrating polymer networks

(IPNs) are a blend of two or more crosslinked polymers that are mutually held together by permanent entanglement.<sup>4</sup> IPN materials have drawn much attention because of the special properties brought about by the interlocking of polymer chains.<sup>5</sup> The interpenetrated system resulting from one crosslinked polymer and one linear polymer is considered a semi-IPN.<sup>6</sup> In the laboratory, grafted or semi-IPN materials from castor oil based polyurethane (PU) and natural polymers such as nitrocellulose,<sup>7</sup> degraded chitosan,<sup>8</sup> nitrochitosan,<sup>9</sup> and benzoyl konjac glucomannan<sup>10</sup> have been synthesized and coated onto regenerated cellulose (RC) films to improve the mechanical properties and water resistance. Interestingly, RC films coated with the IPN coatings can be degraded by microorganisms in soil,<sup>11</sup> accompanied by the production of CO<sub>2</sub>, H<sub>2</sub>O, glucose cleaved from cellulose, aromatic ether from PU, and so forth.

In a previous work,<sup>12</sup> nitrokonjac glucomannan (NKGM), which was prepared from konjac glucomannan (KGM) with a main chain of a  $\beta$ -1,4-pyranoside backbone linked to  $\beta$ -D-mannose and  $\beta$ -D-glucose in an approximate ratio of 1.6:1, was blended with a castor oil based PU prepolymer in the presence of 1,4-butanediol (BD) as a chain-extending agent and diethylenetriamine as a crosslink agent in tetrahydro-

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furan (THF) to synthesize semi-IPNs. The semi-IPNs not only were more easily cured but also had higher tensile strengths than PU when the content of NKGM ( $w_{\text{NKGM}}$ ) was 20 wt %. The effect of the molecular weight of NKGM on the morphology, dynamic mechanical properties, and tensile properties was clarified.<sup>13</sup> The results indicate that NKGM with a weight-average molecular weight ( $M_w$ ) of less than  $8.44 \times 10^4$  plays an important role in the enhancement of the intermolecular interactions between two polymers in semi-IPN sheets. In this case, PU–NKGM semi-IPNs form simultaneously in the presence of PU and NKGM. If the composite ratios of the components are identical, what difference in the structure and properties of the semi-IPN materials will be brought about by different synthesis routes? Furthermore, which synthesis route will be beneficial to the related properties? In this study, NKGM ( $M_w = 4.75 \times 10^4$ ) was mixed with castor oil as a polyol, and the mixture was reacted with toluene diisocyanate (TDI). Using the different preparation methods already mentioned, we attempted to elucidate the difference in the structure and properties between the semi-IPNs obtained in this case and previously. Their structure and optical and mechanical properties were investigated with Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WXRd), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile testing, and ultraviolet spectroscopy.

## EXPERIMENTAL

### Materials

KGM was purified from the plant tubers of *Amorphophallus Konjac* (supplied by Zhuxi Konjac Institute, Hubei, China) according to previous work.<sup>14</sup> NKGM with a degree of substitution of 2.4 and an  $M_w$  value of  $4.75 \times 10^4$  was synthesized according to our previous work.<sup>13</sup>

### Preparation of PU–NKGM

A three-necked flask was fitted with a nitrogen inlet tube, a stirrer, and a pressure-equalizing dropping funnel. The [NCO]/[OH] ratio was predetermined theoretically to be 1.08. Castor oil (4.97 g) and a predetermined amount of NKGM were dissolved in 35 g of butanone with stirring, and then the mixture was concentrated to 20 g by rotary evaporation and poured into the flask. Argon was introduced to the reaction system under reduced pressure. When the temperature was heated to 50°C, 2.53 g of TDI was dropped into the flask within 30 min. The reaction was kept at 50–55°C for 4 h, and then 0.66 g of BD as a chain-

extending agent was added. The reaction was continued for 2 h to obtain the product.

With the addition of butanone, the resulting mixture was adjusted to a solid content of 20% and then was cast onto a glass plate and cured at 60°C for 1.5 h. The plate was immersed in boiling water for 10 min, and the PU–NKGM sheet was peeled off from the glass plate. The sheet was about 100  $\mu\text{m}$  thick. By alterations in the amount of NKGM added in the beginning (0.43, 0.91, 2.04, 3.5, and 5.44 g), a series of sheets containing 5, 10, 20, 30, and 40 wt % NKGM were prepared, and they were coded UNK-II-1, UNK-II-2, UNK-II-3, and UNK-II-4, and UNK-II-5, respectively. The sheet prepared from pure PU was coded PU0, and that from NKGM could not be obtained by a casting method because of its brittleness. The sheets were vacuum-dried at room temperature for 3 days and then were used for the measurements.

### Apparatus and characterization

IR spectra of the samples were recorded with a Nicolet 170SX FTIR spectrometer (Minnesota). The cut sheets were 1 mm long and 1 mm wide, and they were mixed with potassium bromide to make a molded sheet. WXRd patterns of the sheets were recorded on an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Tokyo, Japan) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 30 mA with a scanning rate of 10°/min. The diffraction angle ranged from 5 to 55°. Dynamic mechanical testing of the sheets was carried out by DMA (242, Netzsch, Burlington, MA) under an air atmosphere at a frequency of 1 Hz, a temperature range of –100 to 150°C, and a heating rate of 5°C/min. The sample was 9.0 mm long. DSC tests of the samples were performed with a DSC-2C thermal analyzer (PerkinElmer Co., Boston, MA) under a nitrogen atmosphere (30 mL/min) at a heating rate of 10°C/min from –60 to 150°C.

The light transmittance of the sheets was measured with an ultraviolet–visible spectrophotometer (UV-160, Shimadzu, Kyoto, Japan) over wavelengths of 400–800 nm, and the thickness of the sheets was 100  $\mu\text{m}$ . The tensile strength and breaking elongation of the UNK-II sheets were tested on a versatile tensile tester (CMT-6503, Shenzhen SANS Test Machine Co., Ltd., Shenzhen, China) according to ISO Standard 6239-1986 at a rate of 100 mm/min. The samples were 70 mm long and 10 mm wide, and the distance between two clamps was 50 mm.

## RESULTS AND DISCUSSION

### Structure and miscibility

Figure 1 shows the FTIR spectra of the UNK-II sheets. The absorption bands for the —OH group vibration of

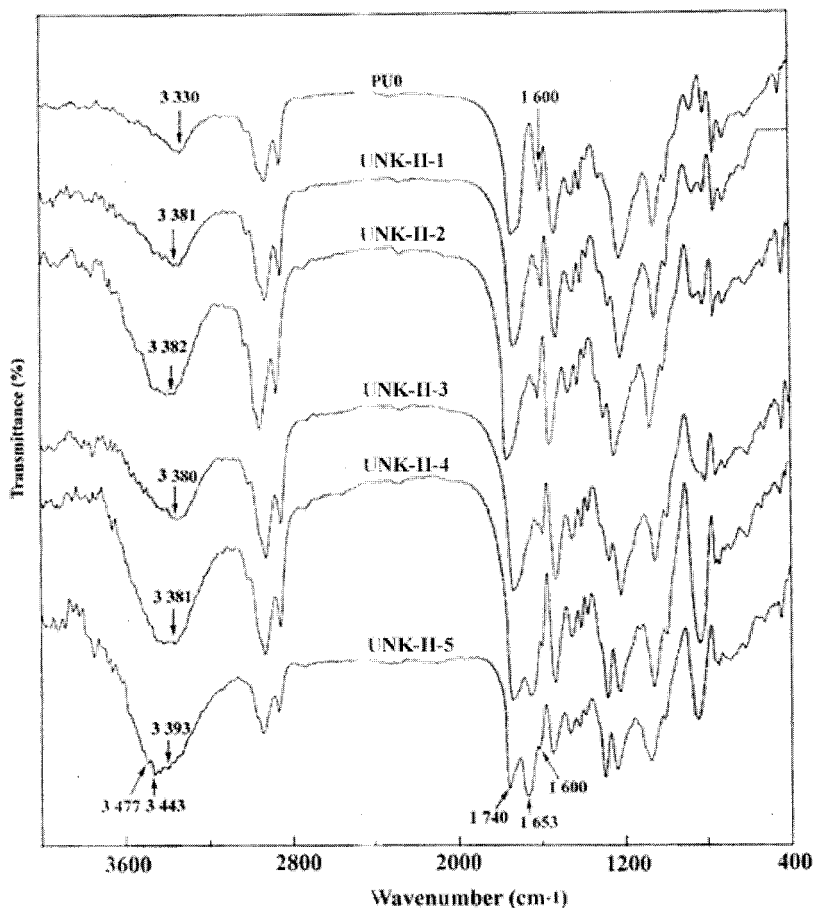


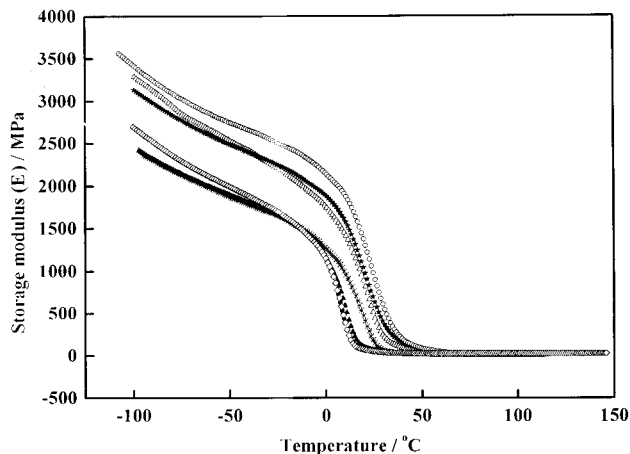
Figure 1 FTIR spectra of UNK-II sheets and pure PU.

UNK-II sheets were broadened, compared with those of PU0. A new stretching band of N—H around 3443 and 3477  $\text{cm}^{-1}$ , absent from the PU0 sheet and assigned to the free N—H groups,<sup>15</sup> appeared in the spectra of the UNK-II series sheets. It indicated that the original hydrogen-bonding interaction in PU was interrupted because of the introduction of NKGM. The bands around 3381  $\text{cm}^{-1}$  for UNK-II-1, UNK-II-2, UNK-II-3, and UNK-II-4 sheets (3393  $\text{cm}^{-1}$  for UNK-II-5) were assigned to the N—H stretching fundamental vibration in Fermi resonance with the carbonyl vibrations.<sup>16</sup> This band was absent from PU. The characteristic absorption bands for —ONO<sub>2</sub> groups around 1653  $\text{cm}^{-1}$ <sup>17</sup> appeared in the spectra of UNK-II-4 and UNK-II-5. The intensity of the typical absorption band for amide II at 1600  $\text{cm}^{-1}$ ,<sup>17</sup> assigned to the bending of —NH groups of NH—C=O groups, gradually decreased with increasing  $w_{\text{NKGM}}$ , and this indicated the occurrence of intermolecular hydrogen bonding between two polymers. Generally, NH—C=O groups are active in forming hydrogen bonding with other polymer chains with polar functional groups.<sup>18</sup> The IR results suggest that interpenetration between NKGM and PU occurred over the course of polymer-

ization of PU, resulting in the formation of a strong intermolecular interaction attributed to hydrogen bonding.

The storage modulus ( $E'$ ) and the ratio of the loss modulus ( $E''$ ) to  $E'$  ( $\tan \delta$ ) were obtained from DMA, and the dependence of  $E'$  and  $\tan \delta$  on the temperature is shown in Figures 2 and 3, respectively. Usually, the main transition ( $\alpha$  transition) reflects the glass-transition temperature ( $T_g$ ) in  $\tan \delta$  spectra.<sup>19</sup> The  $\alpha$  transition of the UNK-II sheets shifted to high temperatures and broadened with an increase in  $w_{\text{NKGM}}$ , indicating that the presence of NKGM in UNK sheets affected the shape and position of the loss peak. The plots of  $E'$  versus temperature showed an enhancement in stiffness for the UNK-II sheets, compared with PU (Fig. 2). At the same temperature, before the onset point corresponding to an abrupt decrease in  $E'$ , the  $E'$  values increased with increasing  $w_{\text{NKGM}}$ , and this indicated that NKGM also played a role in toughness reinforcement.

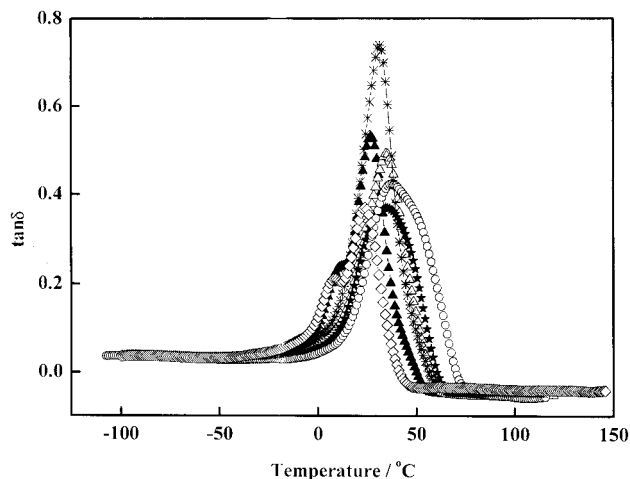
The shape of the mechanical loss peak and the height of the damping peaks ( $\tan \delta_{\text{max}}$ ) can give information about the degree of order and the freedom of molecular motion in the soft domains.<sup>20</sup> Each UNK-II



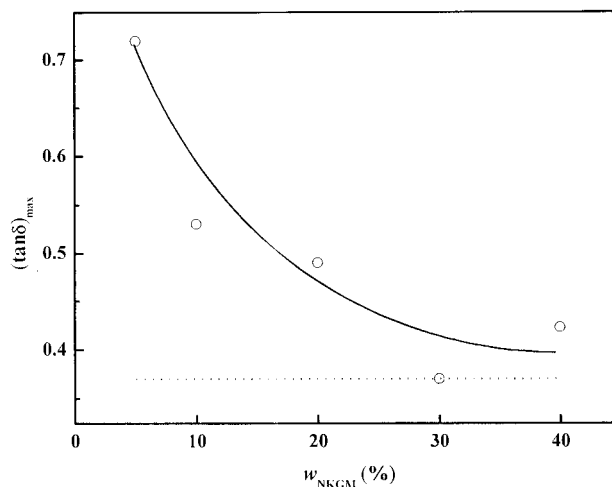
**Figure 2**  $E'$  as a function of temperature for ( $\diamond$ ) PU0, ( $*$ ) UNK-II-1, ( $\blacktriangle$ ) UNK-II-2, ( $\triangle$ ) UNK-II-3, ( $\star$ ) UNK-II-4, and ( $\circ$ ) UNK-II-5.

sheet, except for UNK-II-4, had a higher maximum height of the damping peak ( $\tan \delta_{\max}$ ) than PU, as shown in Figure 4. With  $w_{\text{NKGM}}$  increasing from 5 to 30%, the discrepancy in  $\tan \delta_{\max}$  between the UNK-II series and PU decreased, and this indicated that the motion of soft-segment molecules of PU sharpened with an increase of  $w_{\text{NKGM}}$  because of the degree of microphase separation. The width of half-peaks related to the  $\alpha$  transition ( $W_{\text{half}}$ ; Fig. 5) increased with  $w_{\text{NKGM}}$  increasing from 5 to 40%, suggesting an enhancement in the microphase separation when a large amount of NKGM was intimately entangled. The changes in the shape, position, and intensity of the main relaxation peak indicated a certain degree of phase separation caused by the addition of NKGM.

The DSC thermograms of the UNK-II sheets and PU are shown in Figure 6. Each UNK-II sheet appeared to

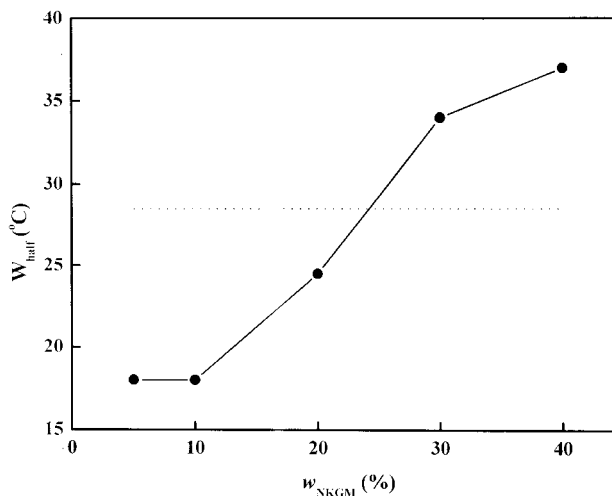


**Figure 3** Mechanical loss as a function of temperature for ( $\diamond$ ) PU0, ( $*$ ) UNK-II-1, ( $\blacktriangle$ ) UNK-II-2, ( $\triangle$ ) UNK-II-3, ( $\star$ ) UNK-II-4, and ( $\circ$ ) UNK-II-5.

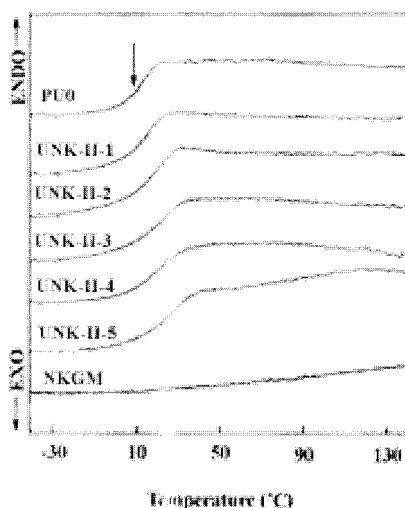


**Figure 4**  $\tan \delta_{\max}$  as a function of  $w_{\text{NKGM}}$  for the UNK-II sheets.

have a glass transition.  $T_g$  from calorimetry corresponds to a relatively large-scale motion of soft segments.<sup>21</sup> The introduction of NKGM into PU resulted in the elevation of  $T_g$  and greater heating capacity changes ( $\Delta C_p$ ) and enthalpy changes ( $\Delta H$ ) in the UNK-II sheets, as shown in Table I, in comparison with PU sheets. This suggests that a certain degree of miscibility existed between NKGM and PU in the UNK-II sheets. Furthermore,  $T_g$  increased steadily with increasing  $w_{\text{NKGM}}$  because the incorporation of the stiff NKGM component led to the restriction of the mobility of PU molecules. The more stiff component there was, the more restricted the chain segment motion was and the higher  $T_g$  was. In this case, NKGM was mixed with castor oil before the polymerization reaction between TDI and polyols. In other words, the PU prepolymer contained linear NKGM. In the previous



**Figure 5**  $W_{\text{half}}$  as a function of  $w_{\text{NKGM}}$  for the UNK-II sheets.

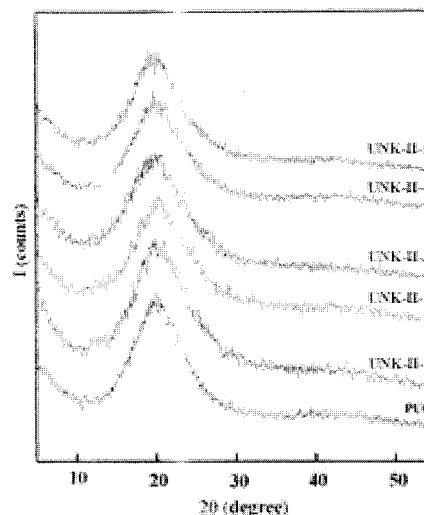


**Figure 6** DSC curves of UNK-II-1, UNK-II-2, UNK-II-3, UNK-II-4, UNK-II-5, and PU0 sheets.

preparation method,<sup>12,13</sup> the addition of NKGM was after the formation of the PU prepolymer. In two preparation methods of semi-IPNs, the concentration distribution of structural units of PU molecular chains was perturbed. Simultaneously, the intermolecular interaction between PU and NKGM occurred because of intimate entanglement and interpenetration. The concentration fluctuation of the PU molecular chain and the restriction of PU molecular motion due to the interaction between two polymers were responsible for the obvious microphase separation between the soft and hard segments of PU. This can be proved by the alterations of  $T_g$ ,  $\Delta C_p$ , and  $\Delta H$  from DSC and by the changes in the shape and position of the damping peaks from DMA.<sup>22</sup> In the previous case,<sup>12</sup> NKGM swelled and interpenetrated into PU when the PU prepolymer and NKGM were mixed in THF, and this interpenetration largely depended on the mixing effect. However, in this case, the degree of the structural change of PU was much greater from the mixing of a linear and rigid polymer with small molecules of castor oil before the polymerization reaction and the formation of the PU network, and the formation of the PU network and semi-IPNs was much harder than in the previous case. NKGM showed no glass transition

**TABLE I**  
Data from DSC Measurements

	$T_g$ (°C)	$\Delta C_p$ (J/°C)	$\Delta H$ (J)
PU	4.79	0.358	13.7
UNK-II-1	5.33	0.442	24.2
UNK-II-2	10.32	0.484	29.3
UNK-II-3	11.16	0.467	32.5
UNK-II-4	12.92	0.388	23.3
UNK-II-5	14.34	0.437	26.5

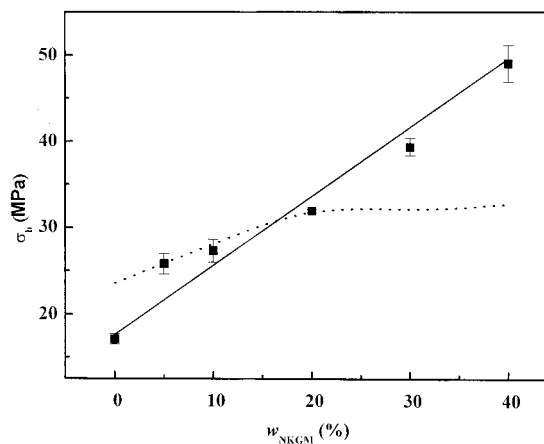


**Figure 7** WXR D diffraction patterns of PU and UNK-II sheets.

in the DSC thermograms, but all the UNK-II sheets and pure PU showed  $T_g$ 's and broad diffraction peaks in their WXR D patterns, as shown in Figure 7, and this indicated an amorphous state.

#### Effect of $w_{\text{NKGM}}$ on the properties

The tensile strength and breaking elongation of the sheets of the UNK-II series and PU are shown in Figures 8 and 9, respectively. The tensile strength of the UNK-II sheets was improved by the addition of NKGM and almost linearly increased with increasing  $w_{\text{NKGM}}$ . However, the breaking elongation of UNK-II sheets sharply decreased with increasing  $w_{\text{NKGM}}$ . Interestingly, with an increase in  $w_{\text{NKGM}}$ , the tensile strength of the PUNK sheets, prepared in a previous work,<sup>12</sup> increased more slowly, and the breaking elon-



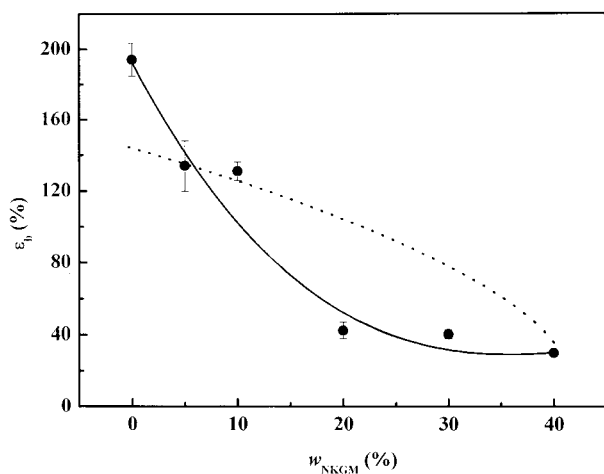
**Figure 8** Tensile strength ( $\sigma_b$ ) of UNK-II sheets as a function of  $w_{\text{NKGM}}$ . The dotted line represents  $\sigma_b$  of PUNK according to ref. 12.

gation also decreased more slowly than that of UNK-II. In particular, when  $w_{\text{NKGM}}$  was lower than 20%, the tensile strength and breaking elongation of the PUNK sheets were both higher than those of UNK-II sheets prepared in this work, and this indicated that the PUNK materials had better miscibility. NKGM is a linear polymer with relatively highly rigid molecular chains, the main chain of which contains two or more  $-\text{ONO}_2$  groups per repeating unit, resulting in intermolecular interactions between two components through hydrogen bonding in the semi-IPN systems. In this work, on the one hand, this interaction enhanced the tensile strength; on the other hand, an increase in the NKGM component proportion resulted in increased stiffness and decreased breaking elongation for the UNK-II sheets.

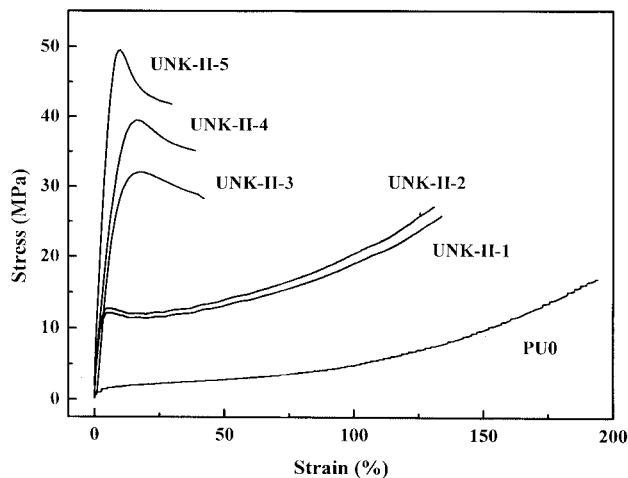
The stress-strain curves of the sheets from tensile testing are shown in Figure 10. The area under the stress-strain curves reflects the toughness of the polymer materials.<sup>23</sup> Obviously, NKGM in the sheets as a strengthening agent mainly played a role in the enhancement of the toughness of the sheets. Interestingly, the curves of the UNK-II-1 and UNK-II-2 sheets showed a yield point. The relatively large area under the stress-strain curves of these two sheets suggested high toughness. A certain degree of microphase separation due to the introduction of a small amount of NKGM was beneficial for improving the mechanical properties of the UNK-II materials. Furthermore, these materials changed from a rubbery state to a plastic state with increasing  $w_{\text{NKGM}}$ .

## CONCLUSIONS

A semi-IPN system is an effective method of obtaining novel biodegradable materials by the interpenetration



**Figure 9** Breaking elongation ( $\epsilon_b$ ) of the UNK-II sheets as a function of  $w_{\text{NKGM}}$ . The dotted line represents the  $\epsilon_b$  of PUNK according to ref. 12.



**Figure 10** Stress-strain curves of UNK-II and PU0 sheets.

of a natural linear polymer into a PU network. In this case, NKGM was mixed with castor oil in butanone first, and then a polymerization reaction between TDI and the polyols was carried out to prepare UNK-II sheets. The dynamic mechanical loss peak of the semi-IPN sheets corresponding to the  $\alpha$  transition of the UNK-II sheets broadened and shifted to higher temperatures with increasing  $w_{\text{NKGM}}$ . A single  $T_g$  appeared in the DSC curve of each UNK-II sheet, and it increased with increasing  $w_{\text{NKGM}}$ . The heating capacity and enthalpy near the glass transition increased in contrast to PU. These results confirmed a certain degree of miscibility between the two components due to the intimate interaction and entanglement of the two polymers. With an increase in  $w_{\text{NKGM}}$ , the tensile strength of UNK-II increased more speedily, and the breaking elongation decreased more speedily than that of PUNK, which was prepared by the simultaneous crosslinking of the PU prepolymer and NKGM and curing in the presence of a chain extender. This indicated that semi-IPN materials prepared by the previous method (PUNK) had better miscibility. However, in the UNK-II materials in this work, NKGM mainly played a role in strength reinforcement, although interpenetration between the two polymers also existed.

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