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Molecular Weight Effects on Properties of Polyurethane/Nitrokonjac Glucomannan Semiinterpenetrating Polymer Networks

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ABSTRACT: Semiinterpenetrating polymer networks (semi-IPNs) were synthesized from castor oil-based polyurethane (PU) and 20 wt % nitrokonjac glucomannan (NKGM) with weight-average molecular weights (M_w) from 2.86×10^4 to 14.1×10^4. Results from the dynamic mechanical analysis, differential scanning calorimetry, wide-angle X-ray diffraction, and ultraviolet spectrometer showed that the semi-IPNs have a single broad α-relaxation peak, one glass transition, and higher optical transmittance (Tr) in the wavelength range of 400−800 nm than PU, suggesting good miscibility in the range of NKGM M_w used. Noted that tensile strength (σ_b) of the semi-IPNs films was much higher than that of films PU and NKGM, and the Tr, σ_b, and breaking elongation (ϵ_b) obviously increased with decrease of NKGM M_w from 8.44×10^4 to 4.75×10^4 (Tr = 88% at 800 nm, $\sigma_b = 34$ MPa, $\epsilon_b = 110\%$). This indicated that the NKGM with relatively lower M_w plays an important role in plasticizing, accelerating cure, and enhancement of intermolecular interaction between two polymers in the semi-IPNs films. The semi-IPNs system provided a novel way for modification and exploitation of natural polymers such as polysaccharides.

Introduction

Recently, naturally occurring polysaccharides were reevaluated as renewable resources because of their environmental friendliness.[1] The present bad environmental situation caused by overburdensome pollutants presses for advancement of materials from renewable resources, which have potential to substitute for some petrochemical products.[2] Konjac glucomannan (KGM), a natural polysaccharide isolated from the plant tuber of *Amorphaphollus Konjac*, is composed of β-1,4-pyranoside back-bond linked β-D-mannose and β-D-glucose in the approximate ratio 1.6:1.[3] A few binary mixtures of konjac glucomannan with other polysaccharides exhibit synergistic interactions which lead to or enhance gelation.[4−6] Abundant hydroxyl groups in konjac glucomannan facilitate the formation of hydrogen bonding with other polymers led to miscibility.[7,8] Moreover, modifications on konjac glucomannan can be carried out by replacing the hydrogen atoms of the hydroxyl groups with others. Thus, KGM has attracted attention, due to its biodegradability, unique reactivity, and water solubility.

In past decades, polymer blends continue to be a subject of intensive investigations in both industrial and academic domains because of the simplicity and effectiveness of mixing two different polymers to obtain new materials.[9] Interpenetrating polymer network (IPN) materials, a kind of mutual polymer blends held together by permanent entanglement between two or more distinctly cross-linked polymers,[10] have drawn much attention due to special properties brought about by interlocking of polymer chains.[11] Polyurethane is a class of very useful and versatile material and widely used as the individual polymer possessing network structure in view of its good flexibility and elasticity. It is worth noting that polyurethane block copolymers based on cellulose derivatives[12] and ligin[13] were realized and proved to be biodegradable. In our recent works, grafted or semi-IPNs materials from castor oil-based polyurethane and natural polymers such as nitrocellulose,[14] elaeostearin,[15] and depolymerized chitosan[16] have been synthesized and coated onto regenerated cellulose (RC) films to improve mechanical properties and water resistance. Interestingly, the RC films coated with the IPNs can be degraded by microorganism in soil, accompanied by producing CO_2, H_2O, glucose cleaved from cellulose and aromatic ether from PU, etc.[17] Therefore, IPNs materials from PU and natural polymers provide a potential application, where biodegradability is important.

In previous work,[18] we prepared a nitrokonjac glucomannan (NKGM) having the degree of substitution of 2.4 and weight-average molecular weight of 4.75×10^4 and used it with castor oil-based polyurethane (PU) to synthesize semi-IPNs. The semi-IPNs not only more easily cure but also have a higher tensile strength than PU when the content of nitrokonjac glucomannan was 20 wt %. In this study, nitrokonjac glucomannan with different molecular weights was prepared. The relationship between weight-average molecular weight (M_w) of NKGM and properties of PU−NKGM semi-IPNs films was clarified. Their structure and optical and mechanical properties were investigated and discussed by light scattering (LS), Fourier transform infrared spectroscopy (FT-IR), wide-angle X-ray diffraction (WXRD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile test, and ultraviolet spectroscopy (UV).

Experimental Section

Preparation of NKGM. To a round-bottomed flask equipped with a mechanical stirrer were added 4 g of KGM purified according to our method[19] from tuber of *Amorphophallus Konjac* (supplied by Zhuxi Konjac Institute in Hubei, China) and a mixture of 100 g of fuming nitric acid, 10 g of sulfuric acid (G. R.), and 40 g of P_2O_5. The flask was placed in an ice bath and cooled for 2 h. Then the reaction was controlled at ambient temperature for desired time. The resulting mixture was poured into excessive water to precipitate the nitrokonjac glucomannan (NKGM). This crude product thus obtained was dissolved with acetone and then was precipitated and washed

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with water three times. After vacuum-drying at 50 °C for 8 h, 3.1 g of white powdered NKGM was obtained. By controlling nitration time for 4, 8, 12, 16, 20, 36, 48, and 96 h, a series of nitrokonjac glucomannan samples coded as NK-1, NK-2, NK-3, NK-4, NK-5, NK-6, NK-7, and NK-8, respectively, were obtained.

Preparation of PU−NKGM. A three-necked flask was fitted with a nitrogen inlet tube, a mechanical stirrer, and a pressure-equalizing dropping funnel. 29 g of toluene diisocyanate (TDI, Wuhan Jiangbei Chemical Reagent Factory in Hubei, China) was poured into the flask. 57 g of castor oil (a chemical reagent with a 4.94 wt % content of hydroxyl groups and hydroxyl value of 163, The Third Chemical Reagent Factory of Zhengzhou in Henan, China) was dropped into the flask under a nitrogen atmosphere at 40 °C. The dropping was completed within 50 min, and then the stirring was maintained at 60 °C for 1.5 h to get PU prepolymer.

The value of [NCO]/[OH] was predetermined theoretically to be 1.08. 3 g of PU prepolymer was mixed with 0.82 g of NKGM with the desired M_w, 0.226 g of 1,4-butandiol (BD) as chain-extending agent, and 0.06 g of diethylenetriamine (DETA) as catalyst in tetrahydrofuran (THF) at room temperature. By adding THF, the resulting mixture was given a solid content (nonvolatile components) of 20%, and then it was cast on a glass plate and cured at 55 °C for 1.5 h to obtain PU−NKGM composite, which was composed mainly of PU and NKGM (8:2 by weight). The plate was immersed in the boiling water for 10 min; then the transparent film of PU−NKGM was peeled off, and the thickness was measured to be 100 μm. The PU−NKGM films prepared from PU prepolymer with NK-1, NK-2, NK-3, NK-4, NK-5, NK-6, NK-7, and NK-8 were coded as UNK-1, UNK-2, UNK-3, UNK-4, UNK-5 UNK-6, UNK-7, and UNK-8, respectively. The film PU was prepared identically except the NKGM addition but cured at 55 °C for 16 h. The curing time of film PU was much longer than that of films UNK. The films were vacuum-dried at room temperature for 3 days and then were used for the measurements.

Characterization. IR spectra of the samples were recorded with a Fourier transform IR (FT-IR) spectrometer (170SX, Nicolet, USA). The films were cut to 1 mm length and 1 mm width and then mixed with potassium bromide to laminate. The content of nitrogen (w_N) in nitrokonjac glucomannan was measured by an element analyzer (CHN-O-PAPID, Heraeus, German). The average degree of substitution of NKGM (DS) was calculated by

$$\mathrm{DS} = \frac{162 w_N}{14 - 45 w_N} \tag{1}$$

Wide-angle X-ray diffraction (WXRD) patterns of the films were recorded on an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Japan) by using Cu Kα radiation ($\lambda = 15.405$ nm) at 40 kV and 30 mA with a scan rate of 10°/min. The diffraction angle ranged from 5° to 55°.

The weight-average molecular weight (M_w) of nitrokonjac glucomannan was determined by using a DAWN-DSP multi-angle laser photometer (Wyatt Technology Co., USA) combined with a pump P100 (Thermo Separation Products) equipped with a TSK-GEL G4000 HHR column (7.8 mm × 300 mm) and a differential refractive index detector (RI-150) at 25 °C. The refractive index increment (d*n*/d*c*) of the nitrokonjac glucomannan in THF measured with a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co.) at 633 nm and 25 °C was 0.093. Astra software was utilized for the data acquisition and analysis.

The dynamic mechanical test of samples UNK was carried out by a dynamic mechanical analyzer (DMA, 242, Netzsch) under an air atmosphere at a frequency of 1 Hz, temperature range of −100 to 150 °C, and heating rate of 5 °C/min. The sample dimension was 9.0 mm long. Differential scanning calorimetry (DSC) of the samples UNK was performed with a DSC-2C thermal analyzer (Perkin-Elmer Co., USA) under a nitrogen atmosphere (30 mL/min) at a heat rate of 10 °C/min from −60 to 150 °C.

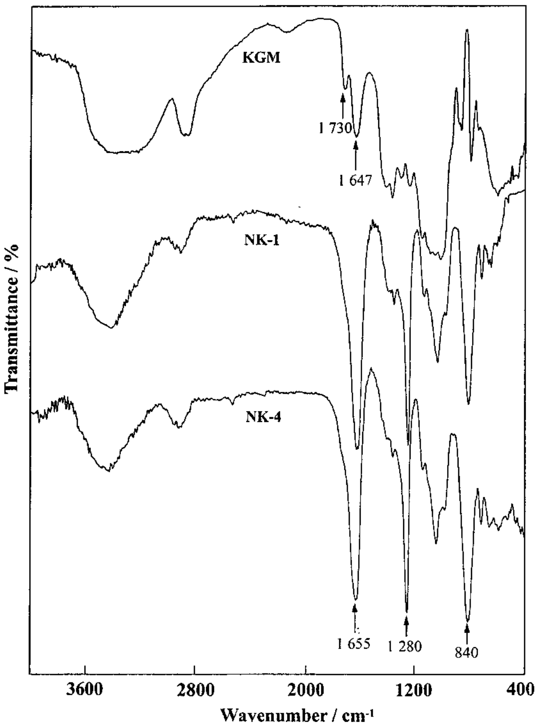

Figure 1. IR spectra of the nitrokonjac glucomannan samples of NK-1 and NK-4.

Tensile strength (σ_b) and breaking elongation (ϵ_b) of the films UNK were tested on a versatile tensile tester (CMT-6503, Shenzhen SANS Test Machine Co. Ltd., China) according to the ISO6239-1986 standard with a rate of 100 mm/min. The size of the samples was 70 mm length, 10 mm width, and 50 mm distance between two clamps.

Optical transmittance (Tr) of the films was measured with a UV−vis spectrophotometer (Shimadzu UV-160, Japan) in the wavelength from 400 to 800 nm, and the thickness of the films used was 100 μm.

Results and Discussion

Structure of PU/NKGM Semi-IPNs. As shown in Figure 1, there are obvious differences in the FT-IR spectra of KGM and NKGM samples. The broad stretching band of −OH groups around 3357 cm^{-1} for KGM is sharply decreased in the spectra of NK-1 and NK-2, indicating the hydrogen atoms of −OH groups in KGM were substituted by $-NO_2$ groups. Accordingly, the three obvious absorption bands at 1655, 1280, and 840 cm^{-1} assigned to $-ONO_2$ groups[20] appeared in the spectrum of NKGM. This indicated that water-insoluble nitrokonjac glucomannan was synthesized. Comprehensive properties of NKGM including nitrogen content, degree of substitution (DS), M_w, and polydispersity ($d = M_w/M_n$) are summarized in Table 1. With the increase of nitration time, the DS value of NKGM increased until it reached around 2.5 for NK-5 to NK-8. The M_w values of NKGM decreased with the increase of nitration time, confirming a gradual depolymerization of konjac glucomannan. The *d* values indicated that NKGM products have a relatively wide molecular distribution and decreased with decrease of M_w.

A series of transparent films UNK were obtained by mixing PU with NKGM with desired M_w in THF solution, suggesting a blend in molecular level, which was clarified by FT-IR in previous work.[18] As mentioned above, NKGM existed in the solution as a linear polymer NKGM was swelled and then interpenetrated into the

Table 1. Nitrogen Content (W_N), Degree of Substitution (DS), Weight-Average Molecular Weight (M_w), and Polydispersity d ($d = M_w/M_n$) of the Nitrokonjac Glucomannan Products

sample no.	W_N/%	DS	$M_w \times 10^{-4}$	d
NK-1	8.65	1.4	14.1	2.87
NK-2	10.39	1.8	10.3	3.68
NK-3	11.45	2.1	8.44	2.95
NK-4	11.58	2.1	7.28	2.54
NK-5	12.74	2.5	6.86	2.73
NK-6	12.79	2.5	5.94	2.31
NK-7	12.48	2.4	4.75	1.79
NK-8	12.91	2.6	2.86	1.53

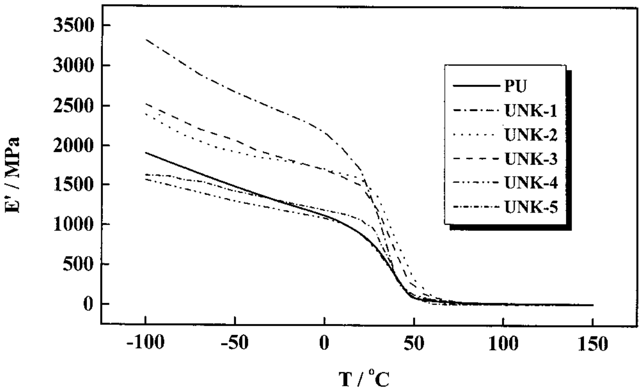

Figure 2. Dependence of storage modulus (E') on temperature (T) in the range −100 to 150 °C for the UNK films.

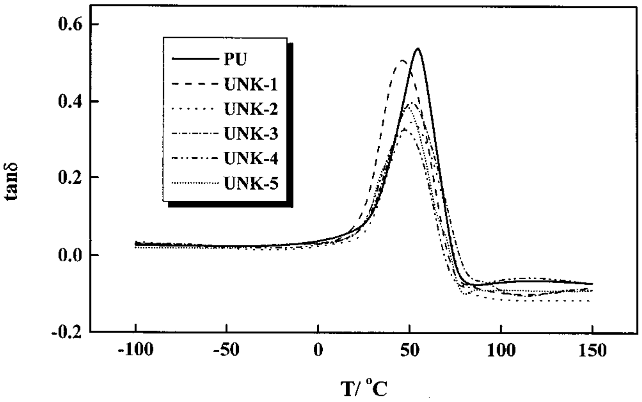

Figure 3. DMA spectra of the films UNK in the temperature range −100 to 150 °C.

PU networks to form interpenetrating network during the thermal curing. Therefore, the films UNK can be referred to as semi-IPNs. IPNs as a kind of novel material resulting from the combination of two or more polymer components have complex internal friction behavior and character, as well as the thermal dynamic incompatibility.[2,21] Morphology and structure of IPNs depend on the method of synthesis and compatibility of the polymer systems employed. DSC and DMA techniques can give information on modulus changes, glass transition behavior, and degree of compatibility.[22,23] The storage modulus (E') and the ratio of loss modulus (E'') to E', tan δ, were obtained from DMA, and the dependence of E' and tan δ on temperature is shown in Figures 2 and 3, respectively. The plots of E' vs temperature showed a drop in stiffness for films, each UNK and PU accompanying the soft-domain glass transition (T_g), as shown in Figure 2. T_g of the films UNK increased with increase of M_w of NKGM except for UNK-1. In view of the sharp slope, E' of each film reached a rubbery plateau around 17 MPa. From a plot of tan δ vs temperature, the presence of NKGM in films UNK strongly affects shape and position of the loss peak. The sharpness and height of the damping peaks [(tan $\delta)_{\max}$] give information about the degree of order and the freedom of motion of molecules in the soft domains.[24] The broadening phenomenon of loss peak shape results from the concentration fluctuation of structural units of molecular chains.[25,26] An explanation for the PU−NKGM composites is that NKGM molecules was dissolved in THF and penetrated into PU network and consequently perturbed the concentration distribution of the original molecules in PU.

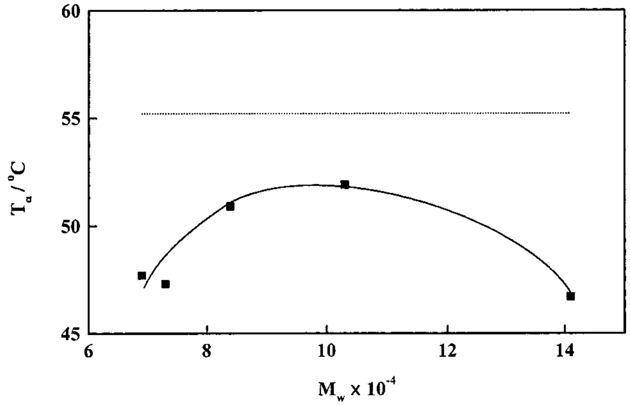

Figure 4. Effect of molecular weights (M_w) of NKGM on T_α of films UNK from DMA spectra. (· · ·) represents T_α of film PU.

The main transition (α-transition) is near the temperature of glass transition (T_g) in tan $\delta - T$ spectra.[27−29] The α-transition always accompanies the strongest mechanical relaxation and the sharpest drop in modulus.[30,31] As shown in Figure 3, the α-transition loss peak appeared for each film UNK was not sharply flattened after NKGM was introduced, implying that the films UNK are all nearly amorphous, which is correlated with the glass transition and damping capacity of the soft domains. The loss peak corresponding to the temperature of α-relaxation (T_α) of the films UNK broadened and shifted to a lower temperature position, compared with the case of PU. These shifts and the broadening of peak shape for the films UNK are featured typically by the polymer composites embodying miscibility. A plot of T_α as a function of M_w of NKGM for the samples UNK is shown in Figure 4. It is obvious that T_α of all films UNK is lower than that of PU, and the great difference between films PU and UNK having the NKGM M_w less than 8 × 10^4 in the T_α exhibited to be above 8 °C. Simultaneously, a similar difference can also be seen from plots of width of half-peak (W_{half}) vs M_w, as shown in Figure 5. Each film UNK has a wider W_{half} than PU. The lowering of T_α and broadening of W_{half} for the films UNK indicated the good phase mixing between the linear NKGM and the PU network.

Interaction between NKGM and PU. It is difficult to obtain the medium point in some of the thermograms.[32] Therefore, the onset temperature was compared in the DSC, and the DSC thermograms of the films PU, UNK, and pure NKGM are shown in Figure 6. T_g of the films UNK from DMA, considered as T_α and shown in Figure 4, differed from the T_g measured from DSC (Figure 6 and Table 2). To illustrate this difference, the nature of DMA and DSC measurements should be referred. The thermodynamic mechanical relaxation of

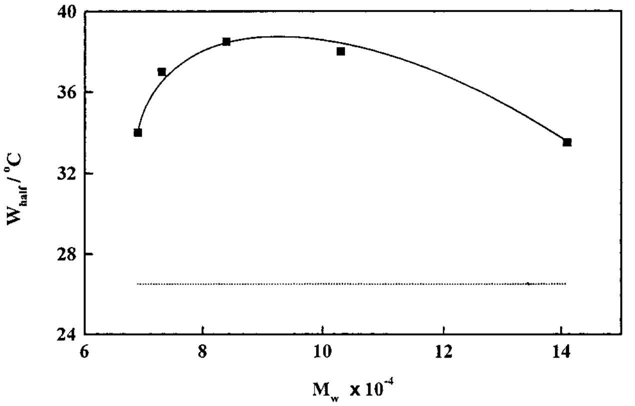

Figure 5. Effect of molecular weights (M_w) of NKGM on W_{half} of films UNK from DMA spectra. (· · ·) represents W_{half} of film PU.

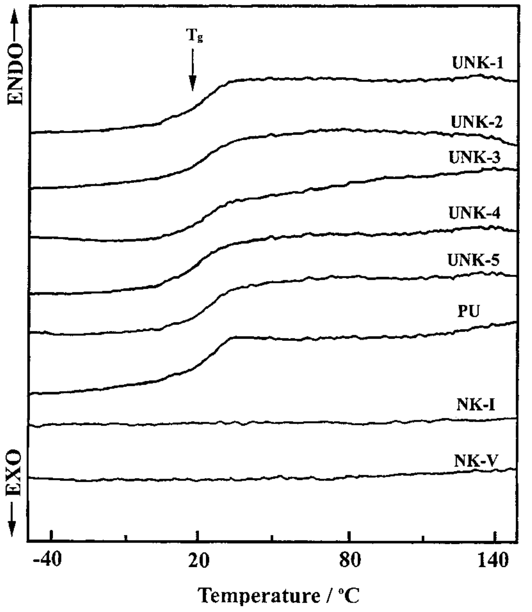

Figure 6. DSC thermograms of the films UNK, PU and pure konjac glucomannan (NK-1 and NK-4).

Table 2. Data from DSC Measurements

film no.	T_g/°C	ΔC_p (J g^{-1} °C^{-1})	film no.	T_g/°C	ΔC_p (J g^{-1} °C^{-1})
PU	17.5	0.401	UNK-3	15.4	0.319
UNK-1	13.6	0.358	UNK-4	17.2	0.392
UNK-2	16.6	0.277	UNK-5	12.2	0.351

DMA results from motion of chain segments, while calorimetry corresponds to a larger scale motion, that is, whole molecules or groups of several molecules.[33] Another explanation for the difference is that DMA measurements reflect the T_g of soft-segment microphase, while DSC measurement records indicate the T_g of pure soft segment.[34] It is noted that NKGM showed no glass transition in the DSC thermograms. However, in the preparation process of the films UNK, the phase structure of the soft segment was changed by adding NKGM in the system before the curing. Moreover, the inducing of NKGM into PU resulted in the reduction of T_g and the heating capacity change (ΔC_p) of the films UNK, compared with film PU (Table 2), suggesting the microphase separation between soft and hard segments.[24,35,36] On the other hand, the single loss peak in the DMA spectra and single glass transition in DSC thermograms imply the great phase mixing between NKGM and PU, resulting in high miscibility in UNK composites in whole. It can be explained that the interpenetrating of NKGM into PU network interrupted the original interactions between soft and hard segments in PU but simultaneously resulted in the stronger interchain interactions between NKGM and PU in the films UNK than that in original PU. However, the interactions between two kinds of polymers were far less than the chemical linkages between the soft and hard segments, which can be proved by decreasing in the values of T_g and ΔC_p for the films UNK, compared with film PU. This downward of T_g of the UNK is known to attributed to the improvement of the degree of freedom for the soft segment in the castor oil-based polyurethane, owing to microphase separation between soft and hard segments.

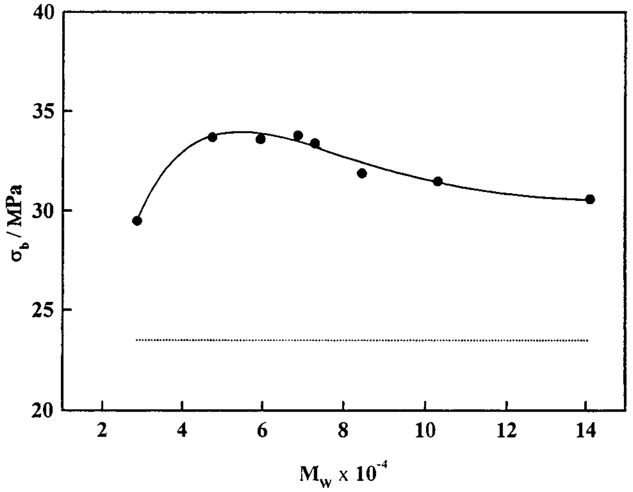

Figure 7. Effect of molecular weights (M_w) of NKGM on tensile strength (σ_b) of films PU and UNK. (· · ·) represents σ_b of PU.

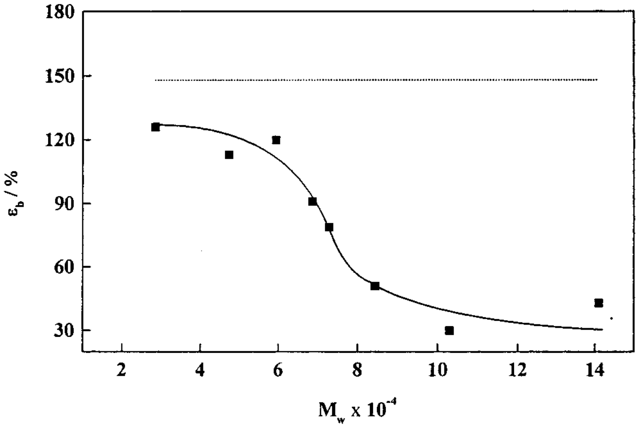

Figure 8. Effect of molecular weights (M_w) of NKGM on breaking elongation (ϵ_b) of films PU and UNK. (· · ·) represents the ϵ_b of PU.

Effects of M_w of NKGM on Properties. The pure NKGM film was so brittle that its mechanical property data cannot be obtained. A plot of tensile strength (σ_b) as a function of NKGM M_w for the films UNK is shown in Figure 7. Great enhancement of σ_b for films UNK in contrast to film PU was observed. This indicated that strong interaction between NKGM and PU occurred in the composites, resulting in the elevation of σ_b. Figure 8 shows that M_w of NKGM strongly affected the breaking elongation (ϵ_b) of films UNK. The ϵ_b values of the films UNK were lower than film PU and steeply

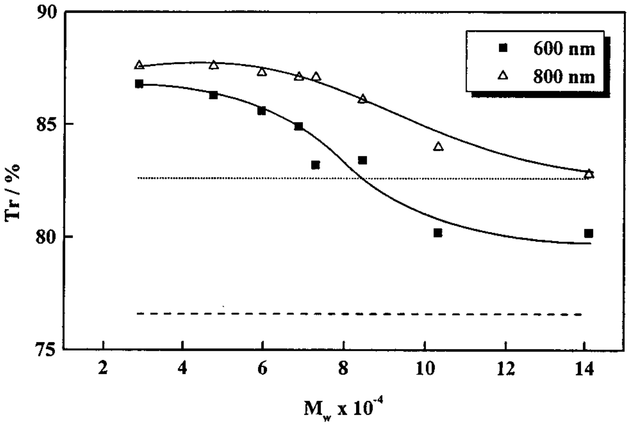

Figure 9. Optical transmittance (Tr) of UNK films in the wavelength region of 600−800 nm. (- - -) and (· · ·) represent Tr of PU at 600 and 800 nm, respectively.

decreased with the increase of NKGM M_w. It should be noted that the three films UNK-6, UNK-7, and UNK-8 having relatively lower NKGM M_w possess the close ϵ_b values to PU. It is incredible for the high flexibility of PU material can be reserved after adding 20 wt % NKGM, a rigid macromolecule. Moreover, both σ_b and ϵ_b of the films UNK obviously increased with decrease of M_w of NKGM from 8.44×10^4 to 4.75×10^4, suggesting that NKGM with relatively low M_w plays an important role in enhancement of mechanical properties. The result from the tensile test was exciting, considering the promising application of this biodegradable material. The enhancement of tensile strength (σ_b) of UNK films (Figure 7) supported the high miscibility in the composite films. The films UNK including NKGM with the relatively low M_w exhibited the higher breaking elongation (ϵ_b) (Figure 8) owing to enhancement in freedom of the molecular motion. Actually, the shifting of T_α to lower temperature, the lowering of $(\tan \delta)_{max}$, and the broadening of W_{half} also revealed the plasticizing effect of NKGM with low M_w (less than 7×10^4) on the films UNK.[37] This plasticizing effect of natural polysaccharide with low molecular weight on castor oil-based polyurethane was also observed in our previous work.[14] So, semi-IPNs system from natural nitrokonjac glucomannan and polyurethane can improve the tensile strength and basically reserved the flexibility of polyurethane.

The optical transparence (Tr) of the composite films UNK is shown in Figure 9. Interestingly, the Tr values of all the films UNK were higher than that of film PU, suggesting the strongest interaction between NKGM and PU by the interpenetrating of NKGM into PU network. Attribution of the good transmittance of polyurethane−polyacrylate IPNs presented by Winnk et al. is due to the match in the refractive indices of the individual polymer components.[38] In addition, the attribution may be correlated with the predominant amorphous state in films UNK. It is obviously Tr values of the films UNK at 600 and 800 nm increased with the decrease of M_w of NKGM, suggesting that NKGM with lower M_w can more easily penetrate into PU network and more intimately blend with PU than that with high M_w. Figure 10 shows the WXRD patterns of films UNK and PU. The appearance of a broad diffraction peak for each film UNK indicated the amorphous nature of the films, supporting the analysis from DMA and UV.

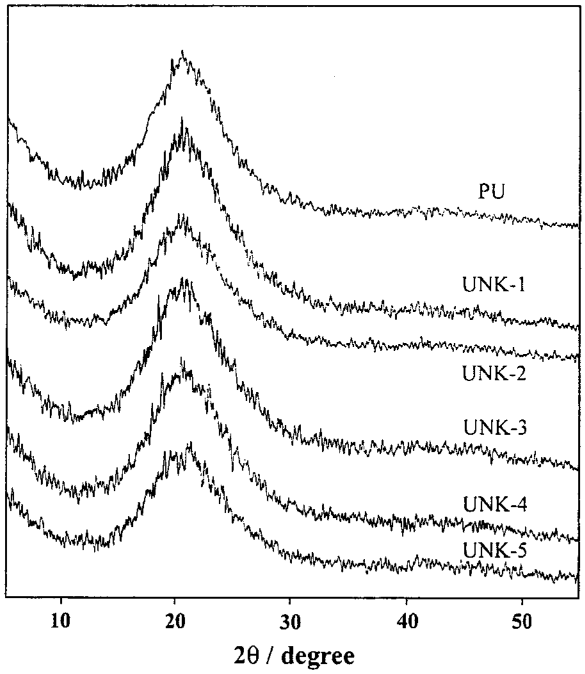

Figure 10. WXRD diffraction patterns of PU and UNK films.

Conclusions

The semiinterpenetrating polymer networks system is an effective method to obtain novel biodegradable materials by interpenetrating linear natural polymer into a PU network. Semi-IPNs films PU−NKGM were prepared by cross-linking the castor oil-based PU prepolymer in the presence of a linear polymer NKGM in THF at 55 °C for 1.5 h. In this case, the linear NKGM dissolved and interpenetrated into PU during thermal curing to form semi-IPNs. The results from DSC, DMA, and optical transmittance indicated that semi-IPNs system in the films UNK had good miscibility in the range of NKGM M_w used in whole. However, inducing NKGM into PU resulted in microphase separation between soft and hard segments, leading to a decrease of T_g and ΔC_p for the films UNK. The tensile strength and optical transmittance of the films UNK were much higher than those of film PU, and the breaking elongation was slightly lowered. They all obviously increased with the decrease of NKGM M_w from 8.44×10^4 to 4.75×10^4. The NKGM with relatively low M_w plays an important role in plasticizing, cure accelerating, and strengthening the semi-IPNs material, owing to strong interaction between two kinds of polymers.

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