

Effects of NCO/OH Molar Ratio on Miscibility and Properties of Semiinterpenetrating Polymer Networks from Polyurethane and Benzyl Konjac Glucomannan

Yongshang Lu, Lina Zhang

Department of Chemistry, Wuhan University, Wuhan, 430072, People's Republic of China

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ABSTRACT: Semi-interpenetrating polymer network (semi-IPN) films with different NCO/OH molar ratios of the urethane prepolymer, coded as UB, were prepared from polyurethane (PU) and benzyl konjac glucomannan (B-KGM) by a casting method. The effect of the NCO/OH molar ratio of the urethane prepolymer on the miscibility and properties of the UB films was investigated using Fourier transform infrared spectroscopy, differential scanning calorimetry, dynamic mechanical thermal analysis, thermogravimetric analysis, and swelling and tensile tests. The results indicated that, with an increase of the NCO/OH ratio, the crosslink density of the UB films increased, resulting in improved miscibility between PU and B-KGM and a relatively high light transmittance of the UB films. However, the thermal

stability of the UB films decreased with increase of the NCO/OH ratio of the urethane prepolymer, due to the depolymerization of the urethane bonds of the PU networks. When the NCO/OH ratio increased from 2 to 4, the tensile strength of the UB films increased from 15 to 27 MPa, while the breaking elongation decreased from 72 to 16%, resulting from the chemical and physical crosslinks, namely, the enhancement of the covalent bonds and hydrogen-bonding networks. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1304–1310, 2003

Key words: interpenetrating networks (IPN); polyurethanes; miscibility

INTRODUCTION

To modify the properties of polymers to meet special needs, considerable interest has been given to interpenetrating polymer networks (IPNs), a special polymer blend, in which two or more polymers are intimately mixed in their networks.^{1–5} Polyurethane has been widely used as an individual polymer, possessing a network structure with good flexibility and elasticity, or as a component of IPNs. In a polyurethane of an $(AB)_n$ molecular structure, *A* represents the soft segment and *B* represents the hard segment, and the soft segment provides flexibility, while the hard-segment units provide physical crosslinks by molecular association through hydrogen bonding.⁶ The inter-

chain attractive force between the hard segments is far greater than that in the soft segments, due to the high concentration of polar urethane linkage and the formation of extensive hydrogen bonding. A polyurethane having different concentrations of the hard segment can be obtained by changing the NCO/OH molar ratio of the urethane prepolymer under a constant content of the soft segment or by changing the chain-extender or crosslinker contents, while keeping the contents of the soft segment and the diisocyanate constant. The effects of a hard-concentration variation in polyurethane of improved miscibility, high modulus, and strength, originating from physically crosslinking or reinforcing the soft-segment matrix with a hard-segment domain, have been reported.^{6–9} In our laboratory, graft-IPNs with NCO/OH molar ratios from 0.73 to 2.0, coded as UL, were prepared from castor oil-based polyurethane and 2.8 wt % nitro lignin, and the UL film with a NCO/OH molar ratio of 1.2 exhibits the maximum value of the tensile strength of 30.2 MPa and the breaking elongation of 152%.¹⁰

Recently, the utilization of renewable resources has drawn much attention because of their potential to substitute for petrochemicals. Konjac glucomannan (KGM), a low-cost polysaccharide consisting of (1→4)-

Correspondence to: L. Zhang (lnzhang@public.wh.hb.cn).

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linked β -D-mannose and β -D-glucose units in a molar ratio of 1.6:1 with a low degree of acetyl groups at the C-6 position obtained from the tubers of *Amorphophallus konjac* plants,¹¹ has been being widely used in food, medical, chemical engineering, and other fields due to its unique physical and chemical properties.^{12–15} In our previous work,¹⁶ a series of semi-IPN films from castor oil-based polyurethane (PU) and benzyl konjac glucomannan (B-KGM) with various contents were successfully prepared. Interestingly, the PU/B-KGM semi-IPNs are good or semimiscible over the entire composition range. The tensile strength of the UB films increased from 7 to 45 MPa with an increase of the B-KGM content from 0 to 80 wt %. The semi-IPN films behaved as reinforced elastomers at a relatively low B-KGM content and as rubber-toughened plastics with a B-KGM content higher than 80 wt %. However, the effects of the hard-segment content on the structure and properties of semi-IPNs has not been understood yet. Here, the semi-IPN films from PU and B-KGM with different hard-segment concentrations were prepared by changing the NCO/OH molar ratio of the urethane prepolymer. Techniques such as Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), ultraviolet spectrometry (UV), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), and tensile testing were used to evaluate the effects of the NCO/OH molar ratio on the structure, miscibility, and properties of the resulting films.

EXPERIMENTAL

Materials and preparation of PU/B-KGM semi-IPNs

All the chemical reagents used here were obtained from commercial resources in China. Purified konjac glucomannan was supplied by the Zhuxi Konjac Institute (Zhuxi, China). The chemical pure castor oil was dehydrated at 100°C under 20 mmHg for 1 h. 2,4-Toluene diisocyanate (TDI) was redistilled before use. *N,N*-Dimethylformamide (DMF) was dried over molecular sieves. The other reagents were used without further purification.

Details of the preparation, purification, and characterization of B-KGM were the same as those in a previous article.¹⁶ The various kinds of isocyanate-terminated castor oil-based PU prepolymers with NCO/OH molar ratios from 2 to 4 were prepared according to the method described by Sperling et al.,¹⁷ and the compositions for the preparation of the semi-IPNs are shown in Table I. The required weights of the PU prepolymer and B-KGM were dissolved in DMF, and then stoichiometric amounts of 1,4-butanediol (1,4-BD) were added as the chain extender. After stirring

TABLE I
Composition of the PU/B-KGM Semi-IPNs

Samples	NCO/OH ^a /OH ^b molar ratio	B-KGM content (wt %)	Hard segment (wt %)
UB-31	2:1:1	20	31
UB-33	2.2:1:1	20	33
UB-35	2.5:1.5:1	20	35
UB-38	3:2:1	20	38
UB-40	3:2.5:1	20	40
UB-43	4:3:1	20	43

^a OH molar number of chain extender.

^b OH molar number of castor oil.

vigorously for 30 min at room temperature, the thoroughly mixed and degassed reactant solutions, whose concentrations were about 20 wt %, were poured into molds. The casting solutions were cured at room temperature for 2 h and then heated to 60°C and held for 4 h to form dry films. The PU/B-KGM semi-IPN films with a thickness of 150 μ m were coded as UB-31, UB-33, UB-38, UB-40, and UB-43, corresponding to the hard-segment content of 31, 33, 38, 40, and 43 wt %, respectively. The samples were dried under a vacuum at room temperature for 2–3 days before testing.

Characterization

Attenuated total reflection infrared spectroscopy (ATR-FTIR) was performed using a 1600 spectrometer (Perkin-Elmer). Samples were taken at random from flat films and data were collected over 16 scans with a resolution of 4 cm^{-1} at room temperature.

DSC thermograms over the temperature range -50 to 200°C were recorded using a DSC-2C thermal analyzer (Perkin-Elmer). The experiments were carried out at a heating rate of $10^\circ\text{C}/\text{min}$, and the sample weights were 17 ± 3 mg. Dynamic mechanical data were collected at 1 Hz with a DMTA-V dynamic mechanical analyzer (Rheometric Scientific) over a temperature range from -50 to 250°C at a $5^\circ\text{C}/\text{min}$ heating rate under a N_2 purge. The specimens were in the form of rectangular strips with a typical size of 10×10 mm (length \times width).

Thermogravimetric analysis (TGA) of the UB films was carried out on a thermal analyzer (TG209, Netzsch Co.) at a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 600°C under an air atmosphere. The weight loss of the UB films at stage I and stage II were calculated by considering the intersection point of the tangents of the TGA curves.

The percent light transmittance of the films with a thickness of 150 μ m was measured using a UV-160A ultraviolet spectrophotometer (Shimadzu, Japan). The tensile strength (σ_b) and breaking elongation (ϵ_b) of the films were carried out on a universal testing machine

(CMT6503, Shenzhen SANS Test Machine Co. Ltd., China) at a crosshead speed of 10 mm/min, and an average value of four replicates of each material was taken.

Swelling test

The crosslink density of the UB films was determined by swelling tests according to the method reported by Yoshida et al.¹⁸ Prior to testing, the UB films were extracted with acetone to free the soluble material. The films of 0.2 g were placed in 20 mL toluene and allowed to stand for 5 days at 25°C. After swelling, the resulting samples were removed from the toluene and weighted after removing the excess toluene. The crosslink density was calculated by

$$\frac{\nu_c}{V_o} (\text{mol/cm}^3) = \frac{-2[\nu + \chi\nu^2 + \ln(1 - \nu)]}{V_1(2\nu^{1/3} - \nu)}$$

where ν_c is the effective molar number of crosslinked chains; V_1 , the molar volume of the solvent; χ , the polymer-solvent interaction parameter; ν , the volume fraction of the dry polymer in the swollen gel ($\nu = V_0/V$); V_0 , the volume of the dry polymer; and V , the volume of the swollen gel at equilibrium.

To determine the χ of the PU/B-KGM semi-IPNs in the toluene system, swelling tests were carried out at 27, 29, 32, and 36°C. From the temperature dependency of the swelling volume, χ values were calculated as follows:

$$\frac{d \ln \nu}{d \ln T} = \frac{-3\chi(1 - \nu)}{5(1 - \chi)}$$

where T is temperature (K) and χ values of the UB films are given as 0.34–0.37. The mean value of 0.35 for the UB films was used to calculate the crosslink density.

The density of the UB films at 27, 29, 32, and 36°C were measured by determining the weight of a volume-calibrated pycnometer filled with a mixture of a NaCl aqueous solution and ethanol, in which the samples achieved floatation level. The density of the sample equals that of the mixture solution.

RESULTS AND DISCUSSION

Effects of NCO/OH ratio on structure and miscibility

The FTIR spectra of the UB films with various NCO/OH molar ratios of the urethane prepolymer are shown in Figure 1. The amide I band in the segment polyurethane systems, which is principally due to carbonyl stretching vibration modes, has a relatively

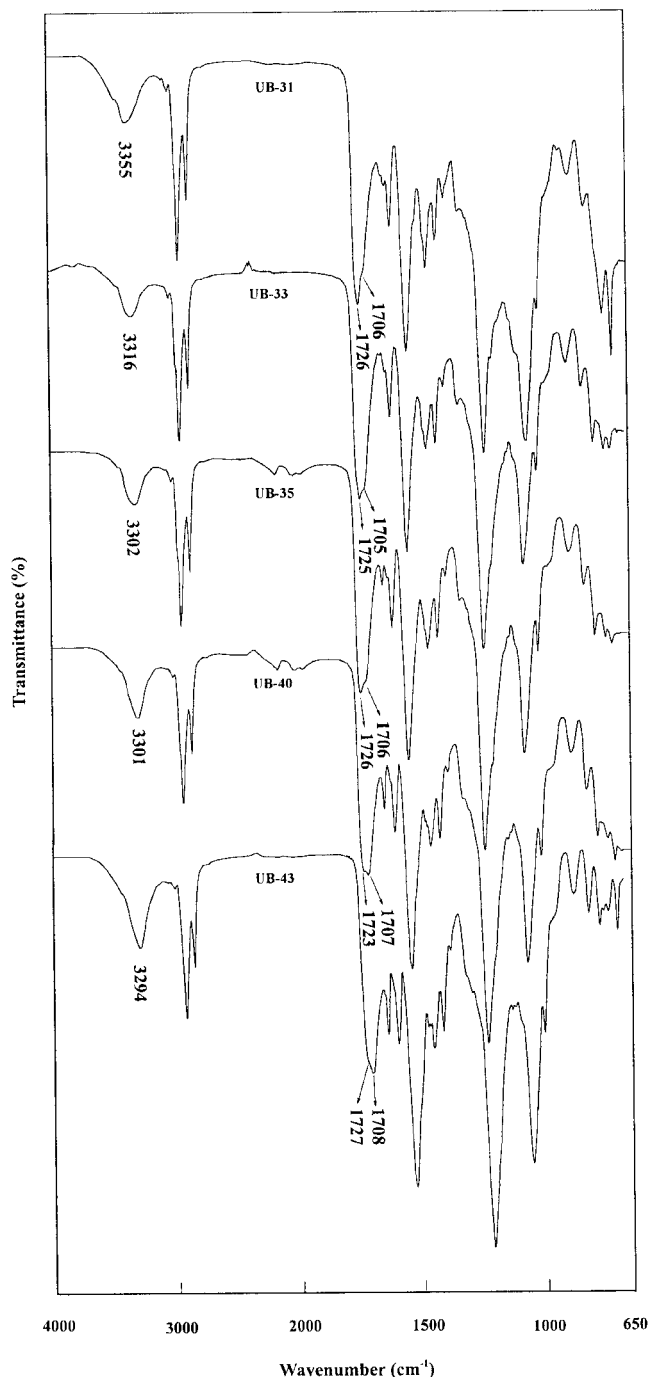


Figure 1 FTIR spectra of the UB films with different NCO/OH molar ratios of the urethane prepolymer.

well-resolved absorption doublet. For the film UB-31, the relative high wavenumber peak at about 1726 cm^{-1} is associated with the nonbonded C=O stretching absorption, and the relative low wavenumber peak at 1706 cm^{-1} represents the absorption of the C=O hydrogen bonded with the NH groups.⁷⁻⁹ With increase of the NCO/OH ratio, the relative intensity of the hydrogen-bonded C=O stretching peak at 1706

cm^{-1} compared with that of the free $\text{C}=\text{O}$ stretching band at about 1726 cm^{-1} increased in the UB films, indicating that the $\text{C}=\text{O}$ was bonded with the NH groups of the hard domains. A peak at 3355 cm^{-1} accompanied by a shoulder peak at a higher wavenumber for UB-31 are attributed to NH-bonded and free NH stretching vibrations, respectively. As the NCO/OH ratio was increased, the shifting of the hydrogen-bonded NH stretching band at $3355\text{--}3294\text{ cm}^{-1}$ was observed. Meanwhile, the intensity of the shoulder peak assigned to the free NH stretching decreased, implying enhancement of the hydrogen-bonded N—H fraction. B-KGM, as linear polymer, penetrated into the three-dimensional PU prepolymer networks in the DMF solutions and then was entrapped into the PU networks to form a semi-IPN structure during the cure process, which was confirmed in our previous works.¹⁶ The hydrogen-bond interactions in the hard domains caused by an increasing NCO/OH ratio can form physical crosslinking networks to improve the mixing between the soft segments and the hard segments, therefore leading to interpenetration between PU and B-KGM.¹⁹

The dependence of the crosslink density and the density of the UB films on the NCO/OH molar ratio of the urethane prepolymer are shown in Figure 2. The crosslink densities of the UB films increased linearly with the NCO/OH ratio, due to the formation of chemical crosslinks resulting from incorporation of more 1,4-BD into the relatively high functional PU prepolymer. The interpenetration between PU and B-KGM in the UB films with a relatively high crosslink density reduced the free volume of the components, resulting in the relatively high density.^{20,21}

The DSC curves of the UB films as a function of temperature are plotted in Figure 3, and the corresponding data are summarized in Table II. The UB-31

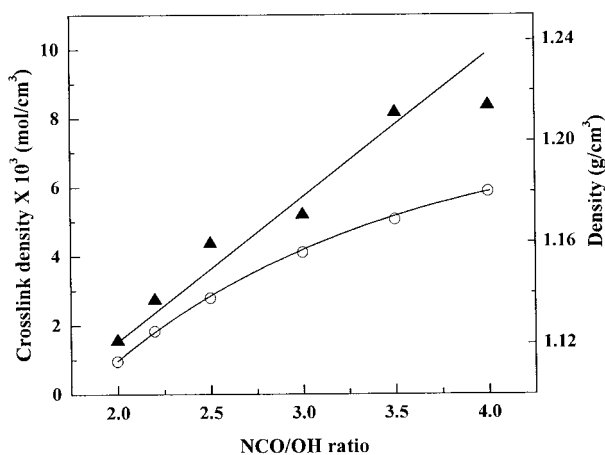


Figure 2 Dependence of the crosslink density (\blacktriangle) and density (\circ) of the UB films on the NCO/OH molar ratio of the urethane prepolymer.

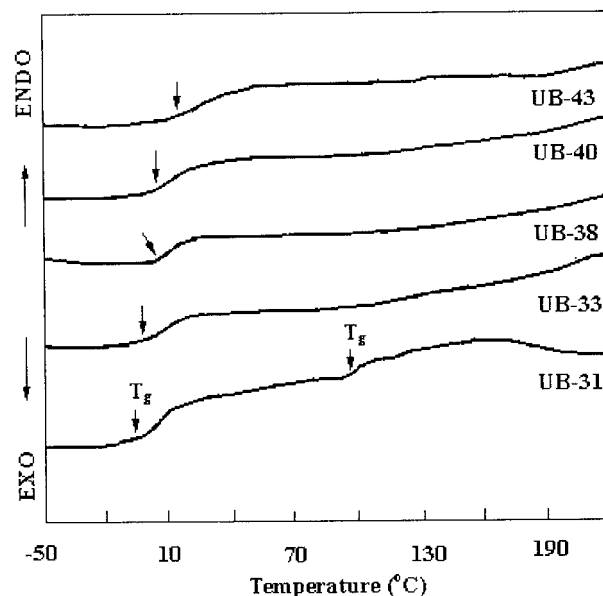


Figure 3 DSC curves of the UB films with different NCO/OH molar ratios of the urethane prepolymer.

film exhibited two glass transition temperatures (T_g 's), corresponding to those of PU and B-KGM (located at 124°C ¹⁶), respectively. This implies that the phase separation occurred between PU and B-KGM. The miscibility between PU and B-KGM can be determined by the shift of the T_g of the films. The disappearance of the T_g for B-KGM and the shifting to higher temperature of the T_g for PU were observed for the UB films with relatively high NCO/OH ratios. This can be explained by that increasing the NCO/OH ratio of the urethane prepolymer can increase the number of urethane groups, resulting in the higher chemical crosslinks of the UB films. Such crosslinks enhanced the microphase mixing between the soft and hard segments of PU and improved the compatibility between PU and B-KGM.^{4,22} Moreover, the UB films showed obvious broader glass transitions as the NCO/OH ratio of the urethane prepolymer increased, indicating a good mixing between the soft and hard segments of PU.⁶

The temperature dependence of the storage modulus (E') for the UB films with different NCO/OH molar ratios of the urethane prepolymer are plotted in Figure 4. Note that the DMA technology generally provides higher T_g values than does DSC due to the dynamic nature of the test.²³ All the UB films exhibited a major relaxation and one rubbery plateau. The significant decreases in the storage modulus for the UB films contributed to the T_g of the PU soft segment. When the NCO/OH ratio increased, the modulus for the UB films increased, due to the restriction of the molecule chain mobility of PU and B-KGM and enhancement of the interconnectivity of the hard-seg-

TABLE II
Data of DSC and DMA of the UB films with Different NCO/OH Ratios of Urethane Prepolymer

Samples	DMA		DSC					
	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)	T_{ge} (°C)	T_{g2} (°C)	T_{gb} (°C)	T_{eb} (°C)
PU	14	—	—	—	—	—	—	—
UB-31	0.8	116	-4.4	-21.5	26.7	99	89.2	114.8
UB-33	15	106	-3.2	-21	31	— ^a	— ^a	— ^a
UB-38	62	—	1.7	-14.4	28.3	—	—	—
UB-40	69	—	4.2	-10.7	43.2	—	—	—
UB-43	75	—	14.9	-3.2	61.1	—	—	—
B-KGM	—	170	—	—	—	124.2 ^b	107.2 ^b	136.9 ^b

T_{gb} , the beginning temperature of the T_g transition region; T_{ge} , the ending temperature of the transition region.

^a Not clearly determined due to the limit of instrument.

^b Results obtained from our previous work (ref. 16).

ment domains. The temperature dependence of the loss peak ($\tan \delta$) for the PU, UB, and B-KGM films is shown in Figure 5. The loss peaks associated with the glass transition and their position and shape can provide information about the degree of phase separation.²⁴ PU and B-KGM exhibited the loss peaks at 14 and 170°C assigned to their T_g transition, respectively. The UB-31 film distinctly showed two $\tan \delta$ peaks, one for each phase, which supports the results from the DSC. The T_g of the UB-31 film, corresponding to that of PU, was even lower than that of the pure PU film. This can be explained by a plasticization effect and by incompetently formed PU networks containing loose chain ends due to incorporation of B-KGM into the PU networks, which enhanced the soft-segment flexibility and mobility. A similar phenomenon was reported for PU/poly(ethyl methacrylate) IPNs.²⁵ For the UB-38 film, the two T_g 's corresponding to the respective com-

ponents both moved inwardly and the PU transition appeared as a shoulder in the broad transition. As the NCO/OH ratio further increased, the UB films such as UB-40 and UB-43 exhibited one $\tan \delta$ broad peak, indicating good miscibility. It is believed that the higher crosslink density caused by the higher NCO/OH ratio of the urethane prepolymer enhanced the compatibility, leading to a strong interconnection between PU and B-KGM.

The light transmittance (T_r) at 800 nm of the UB films with different NCO/OH molar ratios is shown in Figure 6. With increase of the NCO/OH ratio, the T_r values of the UB films increased, indicating the occurrence of enhanced compatibility between PU and B-KGM. If PU and B-KGM were immiscible, namely, the presence of phase separation, the interface between the two polymers will cause losses in the light trans-

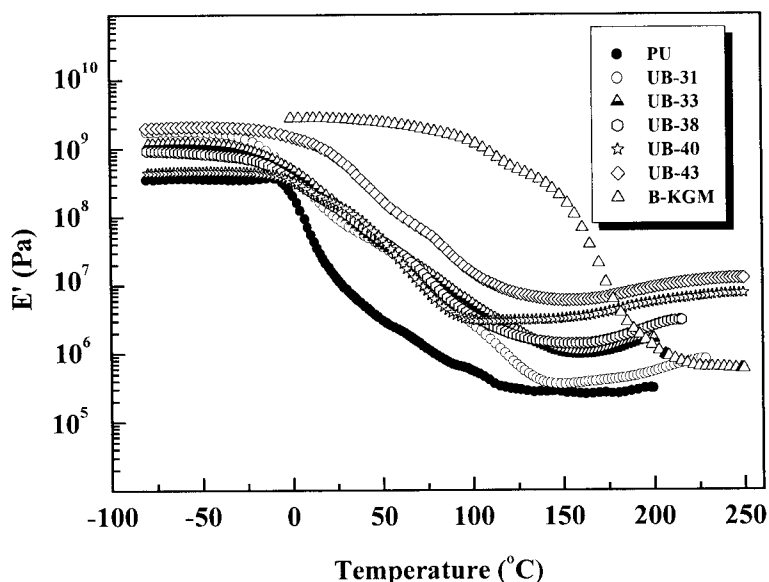


Figure 4 Storage modulus (E') as a function of temperature for the UB films with different NCO/OH molar ratios of the urethane prepolymer.

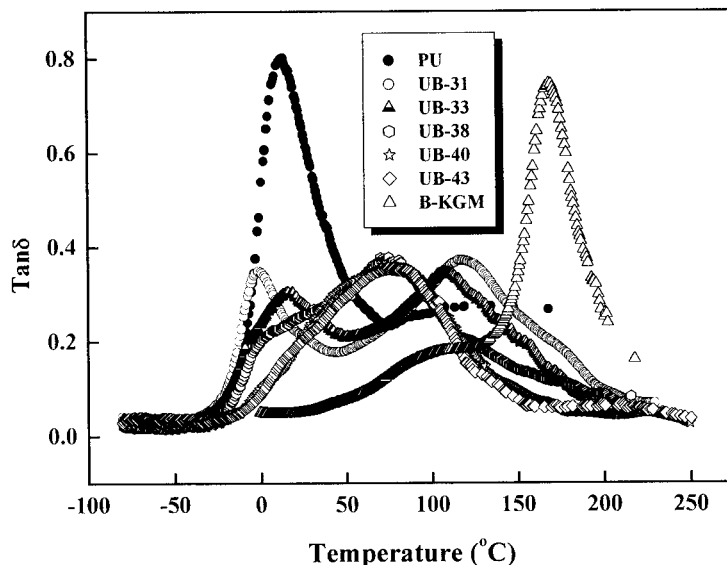


Figure 5 Dependence of $\tan \delta$ on the temperature for the UB films with different NCO/OH molar ratios of the urethane prepolymer.

mittance because of the quality of the light scattered and reflected, resulting in the lower T_r values.^{26,27}

decomposition of polyurethane,²⁸ is indicative of the breakdown of the IPNs by depolymerization at the urethane bonds, resulting in the loss of TDI and

Properties of the UB films

The TGA and DTG traces of the UB films as a function of temperature are shown in Figure 7. All the UB films exhibited two distinct stages of thermal degradation. The first stage of decomposition of the UB films was in temperature region from 270 to 380°C. The weight loss in the first stage increased with an increase of the NCO/OH ratio, which approximately equals the weight of the hard-segment concentration of the respective UB films. This, together with the report on the

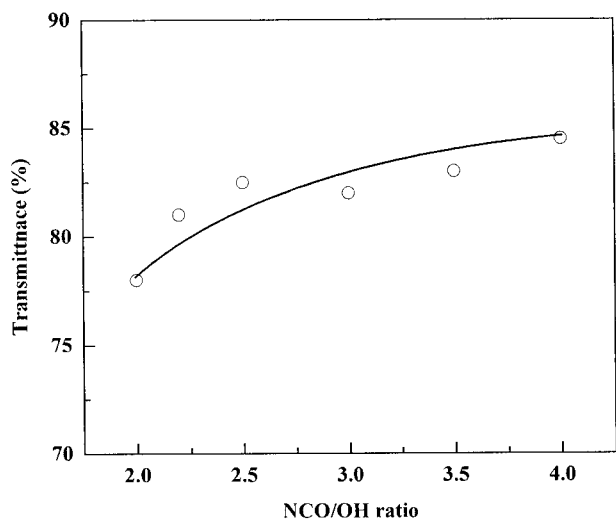


Figure 6 Dependence of light transmittance of the UB films on the NCO/OH molar ratio of the urethane prepolymer.

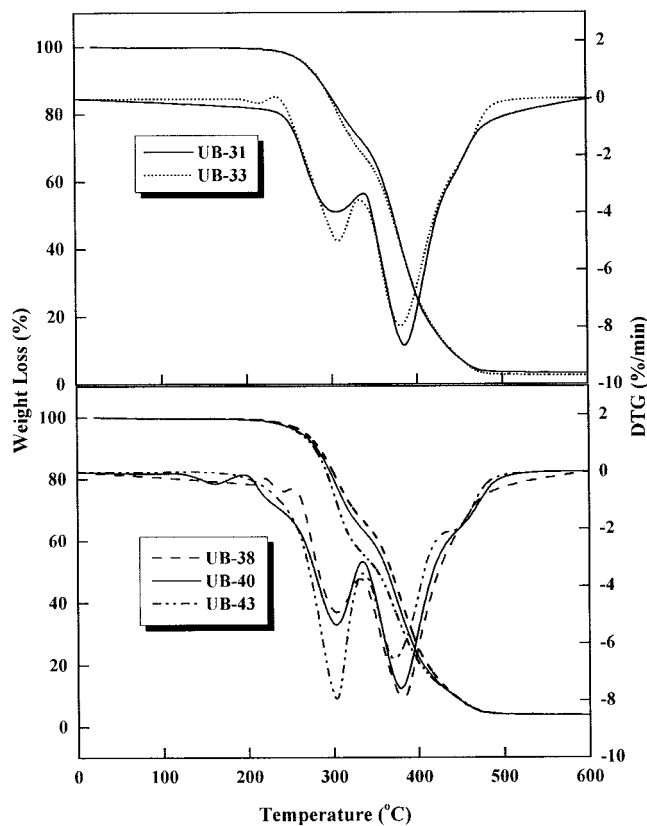


Figure 7 TGA and DTG curves as a function of temperature for the UB films with different NCO/OH molar ratios of the urethane prepolymer.

1,4-BD moieties. The second stage of thermal decomposition, which occurred between 380 to 500°C, is involved probably in some type of chemical reaction, such as main-chain disintegration or rearrangement of some carbon atoms.²⁹ The data of the decomposition temperature and the corresponding weight loss of the UB films are listed in Table III. It is clearly observed that the thermal stability of the UB films decreased with increase of the NCO/OH molar ratio due to the breakdown of the PU networks.

The effects of the NCO/OH molar ratio on the tensile strength and breaking elongation of the UB films are plotted in Figure 8. With an increase of the NCO/OH ratio of the urethane prepolymer, the tensile strength increased from 15 to 27 MPa, while the breaking elongation decreased from 72 to 16%. As the NCO/OH ratio is further increased to more than 4, the resulting materials were too brittle to be tested. Therefore, increasing the chemical crosslinks by an increase of the NCO/OH molar ratio can improve interpenetration and increase intermolecular interaction between PU and B-KGM, which may directly lead to enhancement of the tensile strength and decrease of the breaking elongation.^{4,19}

CONCLUSIONS

The semi-IPNs from castor oil-based PU and B-KGM were prepared by varying the NCO/OH ratio of the urethane prepolymer from 2 to 4. With an increase of the NCO/OH molar ratio, the crosslink density of the UB films increased, resulting in better compatibility between PU and B-KGM. Meanwhile, the mixing between the soft and hard segments of PU was improved due to the enhancing of the hydrogen-bonding interactions as the NCO/OH molar ratio increased. However, the thermal stability of the UB films with a relatively high NCO/OH ratio decreased. With an increase of the NCO/OH ratio from 2 to 4, the tensile strength of the UB films increased from 15 to 27 MPa, while the breaking elongation decreased from 72 to 16%, owing to enhancement of the chemical and physical crosslinks.

TABLE III
Thermal Decomposition Data of the UB Films with Different NCO/OH Ratios of the Urethane Polymer

Samples	Weight loss (%) at various temperature (°C)			Weight loss (%)	
	300	350	400	Stage I	Stage II
UB-31	14.4	32.8	73.7	33.8	62.5
UB-33	15.6	36.2	73.7	35.6	61.8
UB-38	17.3	38.5	74.1	37.3	59.0
UB-40	20.2	42.1	77.2	41.8	54.5
UB-43	23.1	49.1	79.2	42.2	54.6

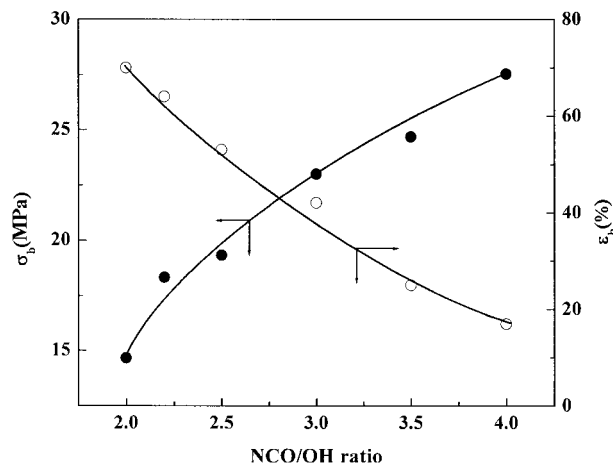


Figure 8 Dependence of mechanical properties of the UB films on NCO/OH molar ratio of the urethane prepolymer.

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