

Effects of Nitrolignin on Mechanical Properties of Polyurethane–Nitrolignin Films

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ABSTRACT: Polyurethane-nitrolignin (PUNL), a new network polymer, was synthesized from a castor oil based–polyurethane(PU) prepolymer and nitrolignin (NL) with a weight-average molecular weight of 20.6×10^4 and a content of 1.4–10%. The structure and miscibility of PUNL films prepared by solution casting were investigated by infrared spectroscopy and transmission electron microscopy. The results indicated that PUNL2 film, which had a 2.8% NL content, was the most miscible, and its tensile strength (σ_b) and breaking elongation (ϵ_b) were 2 times higher than that of PU film. The crosslink densities of PUNL films increased with the increase of NL content until about 3%, similar to the variety of the mechanical properties. Thermogravimetric analysis revealed that the thermal stability of PUNL films was slightly higher than that of PU. Covalent bonds occurred between PU prepolymer and the NL in the PUNL films, forming crosslink networks, which resulted in the enhancement of mechanical properties and thermal stability. NL has a far higher reactivity with PU than nitrocellulose. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1213–1219, 2001

Key words: nitrolignin; polyurethane; mechanical properties; crosslink network; thermal stability

INTRODUCTION

Nearly 200 million tons of plastics materials are now manufactured each year for a global population approaching 6 billion. These activities consume 4% of the raw oil extracted from the earth annually.¹ Therefore, there is increasing interest in the use of renewable resources because of their potential to substitute for some petrochemical products and to decrease the environmental pollution caused by nonbiodegradable polymers. Cellulose and wood are most abundant in nature and are renewable, biodegradable, biocompatible, and derivatizable, offering many possibilities for var-

ious uses.² Lignin is a nontoxic, commercially available, and low-cost renewable resource that has the potential to be utilized as a basic raw material in the chemical industry.³ The millions of tons of lignin produced each year as a by-product of papermaking present a major supply of biomass raw material.⁴ About 750,000 tons of lignin, mainly water-soluble lignin sulfonates, have been used annually worldwide for various industrial purposes, but attempts to expand the application of lignin into other areas have been not very successful because of performance deficiencies shown by technical lignin and lack of a fundamental understanding of the structure–property relationship of lignin.⁵ The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl, and *p*-hydroxyl phenol) are bonded together by a set of linkages to form a very complex matrix.⁶ The reported developments of lignin are

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based on lignin-graft copolymers, lignin-thermo-setting polymers, and lignin-elastomer systems.³ Lignin, with its many reactive hydroxyl groups, can react with isocyanates to form urethane,⁷ and polyethoxylated methacrylates have been grafted on lignin.⁴ Moreover, lignin can be used as a natural polyol to prepare polyurethanes, such as polyurethane foams from carboxylated lignin,⁸ polyurethane engineering plastics from hydroxypropyl lignin,⁹ and polyurethane films from kraft lignin.⁵

Interpenetrating polymer networks (IPNs) usually take on a homogeneous mixture of the component polymers, such as polyurethane and others. Castor oil is also one of the natural polyols most useful for the synthesis of the polyurethane phase in IPNs because of its three reactive hydroxyl groups. IPNs based on castor oil polyurethane (PU) with synthetic polymers, such as polystyrene,¹⁰ acrylates,^{11–13} poly(ethylene terephthalate),¹⁴ and resin,^{15,16} have been successfully prepared to improve the structure and properties of the materials. The grafted, semi-, and full-IPN coatings from PU with natural products, such as depolymerized chitosan¹⁷, nitrocellulose,¹⁸ and elaeostearin,¹⁹ have been satisfactorily synthesized in our laboratory, exhibiting excellent mechanical properties and biodegradability.^{17–20}

Based on the information mentioned above, we attempted to introduce nitrolignin (NL) into PU in order to gain a fundamental knowledge of the chemistry and physics of the network formation for lignin derivatives and of the effects of NL on the properties. In this study polyurethane-nitrolignin (PUNL) films were prepared from castor oil based-polyurethane and nitrolignin by solution casting. The basic characteristics of nitrolignin, such as molecular weight and structure, were measured. The structure, miscibility, mechanical properties, and thermal stability of PUNL films were investigated.

EXPERIMENTAL

Materials

All the chemical reagents were obtained from commercial resources in China. Chemically pure castor oil was dehydrated at 100°C under 20 mmHg for 1 h. Alkali lignin from bamboo was supplied by Guangzhou Chemistry Institute of China. 2,4-Toluene diisocyanate (TDI) was redis-

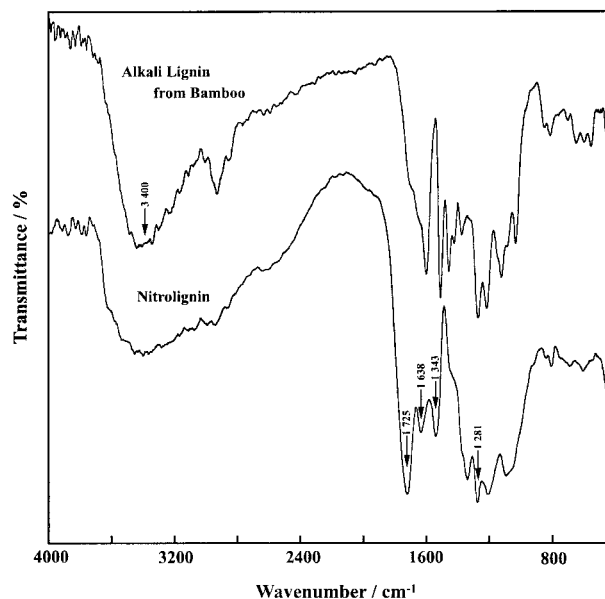


Figure 1 FTIR spectra of alkali lignin from bamboo and its nitroderivative.

tilled before use. The 1,4-butanediol (BDO) was chemically pure.

Preparation of Polyurethane-Nitrolignin Films

The creation of nitrolignin (NL) was achieved by reacting alkali lignin with nitrosonitric acid and acetic anhydride added by droplet under an ice/salt bath for 12 h with stirring. After the reaction the solid precipitate was removed by ultracentrifugation, then washed with water until neutral, followed by drying in vacuum for 7 days to obtain the reddish-brown powder. The N content of NL was determined to be 6.32% by element analyzer (Carlo Erba Strumentazione MOD-1106, Italy). The FTIR spectra of the alkali lignin before and after nitration were obtained by using Fourier Transform Infrared Spectrometer (Nicolet 170SX) and are shown in Figure 1. After nitration the novel absorptions at 1725, 1638, and 1281 cm^{-1} ($-\text{N}=\text{O}$ or $-\text{O}-\text{NO}_2$) appeared, and the intensity of peak at 3400 cm^{-1} ($-\text{OH}$) obviously weakened, indicating successful synthesis of NL.

The weight-average molecular weight (M_w) of NL was measured by using a multiangle laser photometer equipped with a He-Ne laser of $\lambda = 633 \text{ nm}$ (DAWN-DSP, Wyatt Technology Co., Santa Barbara, CA) in tetrahydrofuran (THF) at 25°C and 18 angles. The NL solutions ($c = 0.88 \sim 4.45 \times 10^{-3} \text{ g mL}^{-1}$) were filtered with a series of filters (0.45, 0.20, and 0.20 μm , Whatman) di-

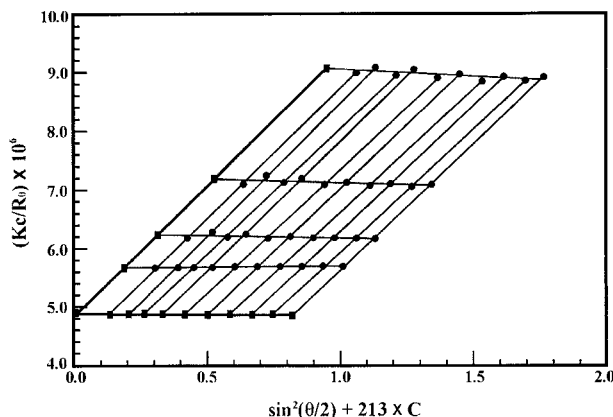


Figure 2 Zimm plot of nitrolignin in THF at 25°C.

rectly into a scintillation vial. The refractive index increment (dn/dc) was obtained on a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co.) at 633 nm and 25°C and determined to be 0.149 mL g^{-1} for NL in THF. Astra software was utilized for the data acquisition and analysis, and the Zimm plot of NL in THF at 25°C is shown in Figure 2. The measured value of M_w for NL is 20.6×10^4 . The intrinsic viscosity $[\eta]$ of NL in THF at 25°C was determined by Ubbelohde viscometer to be 4.42 mL g^{-1} . The $[\eta]$ value was much lower than for normal polymers with the same M_w , suggesting that NL in THF is a dense random conformation, similar to the Einstein sphere, because of its highly branched and networked structure.

Castor oil based-polyurethane (PU) prepolymer (NCO:OH = 2.0, molar ratio) was prepared according to the method described by Sperling.¹⁰ Into THF were dissolved 3.0 g of PU prepolymer, NL of various weights, and 0.45 g of BDO as a chain extender, which was then mixed at room temperature for 15 min. The concentrations of the components in the mixture were about 18.2% for the PU prepolymer, 2.8% for BDO. The resulting mixture was cast on a Teflon plate to form film and then cured at 20°C until there was complete evaporation of the THF solvent, forming dry film. According to the weight of the added nitrolignin (noted in parentheses), the films were coded as PU (0 g), PUNL1 (0.05 g), PUNL2 (0.1 g), PUNL3 (0.2 g), PUNL4 (0.3 g), and PUNL5 (0.4 g), exhibiting colors from golden yellow to reddish brown (PU was light yellow). PUNL films possessed preferable resistance to distilled water, acid (25% H_2SO_4 and 25% CH_3COOH), and alkali (5% NaOH), in which the weight loss was verified by

only about 1.11–4.82%. To study the effect of cured temperature on the mechanical properties, a series of films cured at 35°C and 50°C were also prepared.

Characterization

FTIR spectra of PU and PUNL films were taken by the KBr method using a Fourier Transform Infrared Spectrometer (Nicolet 170SX) in a wavenumber range of 4000–400 cm^{-1} . Transmission electron microscopy (TEM) of PU and PUNL2 films was done with an electron microscope (JEM 100-XT), using the method previously described.²¹ The mechanical properties [tensile strength (σ_b), breaking elongation (ϵ_b), and Young's modulus (E)] of PU and PUNL were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., China) running at a rate of 100 mm min^{-1} according to the Chinese standard method (GB4456-84). Thermogravimetric analysis (TGA) curves for PU and PUNL films were recorded on a DT-40 thermogravimetric analyzer (Shimadzu Co., Japan) under a nitrogen atmosphere with a flow capacity of 30 mL/min from 20 to 600°C at a heating rate of 10°C min^{-1} .

Swelling Test

The crosslink density of the samples of PU and PUNL films was determined according to the method reported by Yoshida.⁵ Prior to the testing, the samples were freed from soluble materials by extraction with acetone. To obtain the crosslink density of the films, three pieces of film about 0.2 g each were placed in 30 mL of dimethylformamide (DMF) and allowed to stand for 7 days at 25°C. The swelled films were removed from solvent and absorbed of excess DMF with a filter paper, then reweighed. The crosslink density may be calculated by

$$\frac{v_c}{V_0} = \frac{-2[v + \chi v^2 + \ln(1 - v)]}{V_1(2v^{1/3} - v)} \quad (\text{mol/cm}^3) \quad (1)$$

where v_c is the effective molar number of crosslinked chains, V_1 is the molar volume of solvent, χ is the polymer-solvent interaction parameter, v is the volume fraction of polymer in swollen gel ($v = V_0/V$), V_0 is the volume of dry polymer ($V_0 = w/\rho$), and V is the volume of swollen gel at equilibrium. To determine the χ for the PU or PUNL in the DMF system, swelling tests were carried out at 25°C, 29°C, 33°C, and 37°C. From

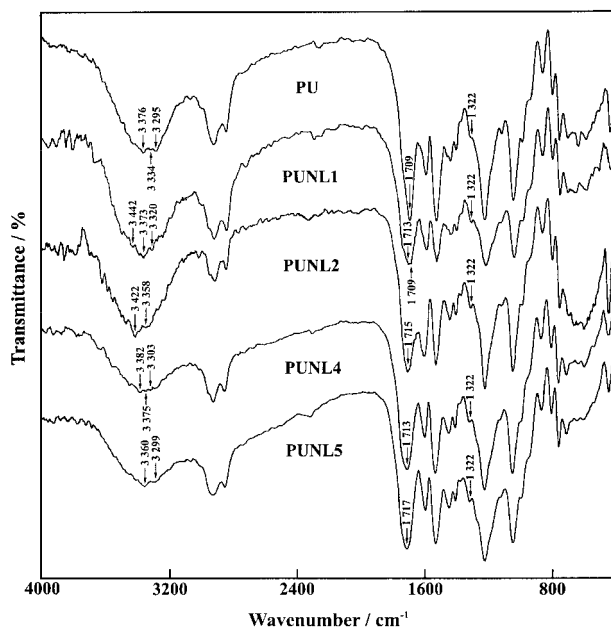


Figure 3 FTIR spectra for PU and PUNL1, PUNL2, PUNL4, and PUNL 5 films.

the temperature dependence of the swelling volume, χ values were calculated as follows:

$$\frac{d \ln v}{d \ln T} = \frac{-3(1 - v)}{5(1 - \chi)} \quad (2)$$

where T is the temperature (K). χ values of PU and PUNL films were given as 0.47 and 0.43~0.47, respectively, while 0.47 for PU and the mean value 0.45 for PUNL were used to calculate the crosslink density. In this study the weight percent of NL in PUNL films was small, so the difference in the χ values for the films was negligible.

The density (ρ) of the samples of PU and PUNL films was measured at 25°C, 29°C, 33°C, and 37°C by determining the weight of a volume-calibrated pycnometer filled with a mixture of ethanol and chloroform in which the samples achieved flotation level. The density of the sample equaled the mixture density.

RESULTS AND DISCUSSION

Structure and Miscibility of PUNL

The FTIR spectra of PU and PUNL films are shown in Figure 3. The infrared spectroscopy (IR) spectrum of PU films shows the characteristic

absorption band at 1709 cm^{-1} , assigned to the hydrogen-bonded urethane carbonyl groups²² in PU film, while a new absorption band at about $1713\text{--}1717 \text{ cm}^{-1}$ appeared in the IR spectra of PUNL films but was absent in both the nitro lignin and the PU spectra because of the superposition of a new band (1725 cm^{-1}) of the aromatic ester bonds, formed by nitro lignin with PU prepolymer and the band at 1709 cm^{-1} of PU. Moreover, the bands of ester bonds at 1322 cm^{-1} for PUNL films were slightly stronger than those for PU film, indicating that esterification between nitro lignin and PU prepolymer had taken place. With the increase of NL content, the —NH stretching vibration bands at 3400 cm^{-1} of PU and PUNL films changed. The bands between about 3422 and 3442 cm^{-1} assigned to free —NH in PUNL1 and 2 films obviously had become more intense than PU, indicating that the interpenetration and reaction of nitro lignin had broken the inter- and intramolecular hydrogen bonds of PU. In addition, in the IR spectra of PUNL films, there was a weakening in the band at 3334 cm^{-1} assigned to the hydrogen bond caused by —NH in PU. This indicates that a suitable mass of NL can easily react with PU into the networks and destroy the original hydrogen bonds in PU.

TEM images of PU and PUNL2 films are shown in Figure 4. The PUNL2 film displays a black boundary region in a two-sided surface. This may be that the enhanced density of the surfaces for the PUNL2 film as a result of the acceleration of the NL crosslink with PU under air. The smooth surfaces for the PUNL2 film, which are consistent with its transparent appearance, show that the PU–NL blend is homogeneous—that is, it has good miscibility, which may be attributed mainly to the low content of NL in the network.

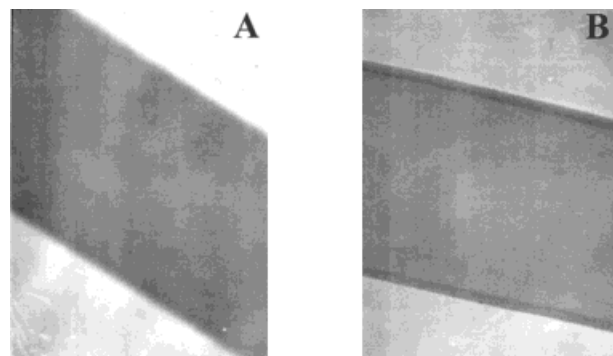


Figure 4 TEM images for (a) PU and (b) PUNL2 films.

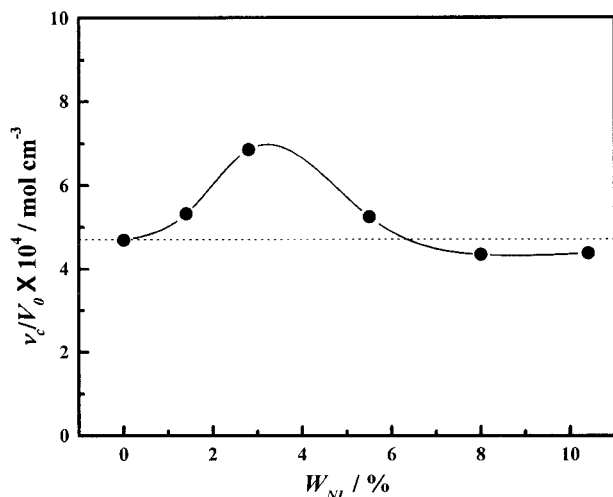


Figure 5 Effect of NL content (W_{NL}) on the crosslink density at 25°C for PUNL films cured at 20°C. (· · · · ·) represents the crosslink density of PU film.

In Figure 5 the crosslink densities of PU and PUNL films were plotted as a function of NL content. It was observed that the crosslink densities of PUNL films increased with an increase of NL content up to 2.8% and then decreased and that they were higher than that of the PU film except for the PUNL4 and PUNL5 films. This indicates that a suitable content of NL plays an important role in the promotion of the PU network formation, resulting in the enhancement of the crosslink density in the PUNL films. This result is supported by the conclusion deduced from the IR spectra, namely, that covalent bonds between PU and NL occurred.

Effect of NL Content on Mechanical Properties

Figure 6 shows how the NL content is dependent on the tensile strength (σ_b) and breaking elongation (ϵ_b) of PU and PUNL films at various cured temperatures. Both the σ_b and ϵ_b of PUNL films increased with an increase of NL content up to about 2.8% and then decreased, similar to the effect of NL content on crosslink density. It was observed that PUNL films with a content of NL above 8% exhibited lower tensile strength and breaking elongation than PU film, indicating that excessive NL hindered the reaction between PU and NL. Interestingly, the introduction of NL, which is stiffer than PU, resulted in an acute increase of breaking elongation, proving further network formation between PU and NL. The cured temperature had some influence on the me-

chanical properties, and the optimal cured temperature was evaluated as 35°C. Figure 7 shows the stress-strain curves of PU and PUNL films cured at 20°C. Compared with PU, the strain-stress curves of PUNL films did not show the yield point that represents the transition from rubber to plastics, suggesting a rubberlike PUNL. It is worth noting that both the tensile strength and breaking elongation of the PUNL films were 2 times higher than that of PU film. This can be explained by the suitable crosslink network between two polymers in PUNL films enhancing the strength and toughness of the material. Figure 8 shows the NL content dependence of Young's modulus of PU and PUNL films. When NL content was more than 2.8%, the Young's modulus of PUNL films increased with an increase of NL

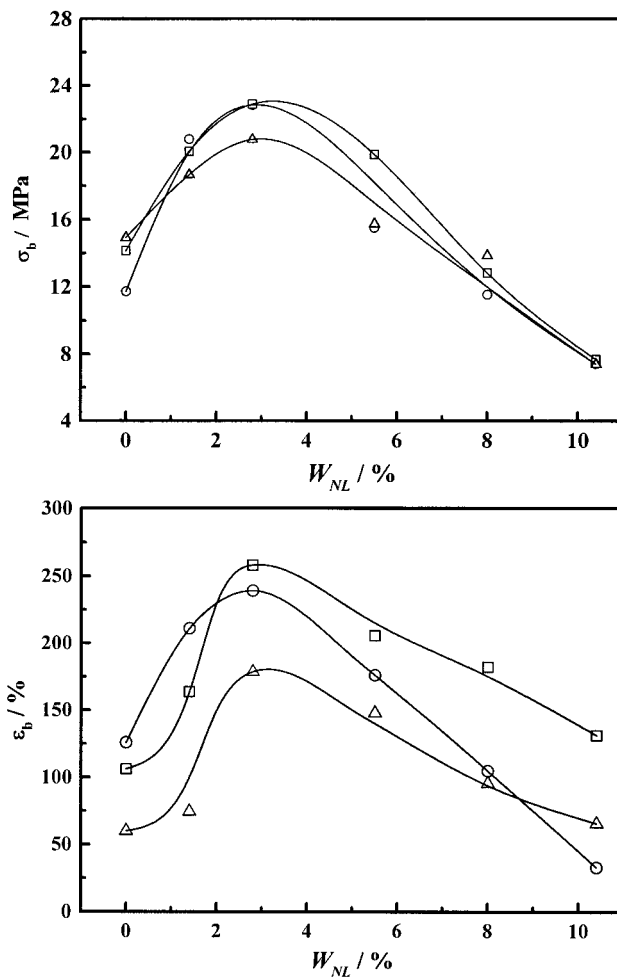


Figure 6 Effect of NL content (W_{NL}) on tensile strength σ_b (up) and breaking elongation ϵ_b (down) for PU and PUNL films at cure temperature of (○) 20°C, (□) 35°C, and (△) 50°C.

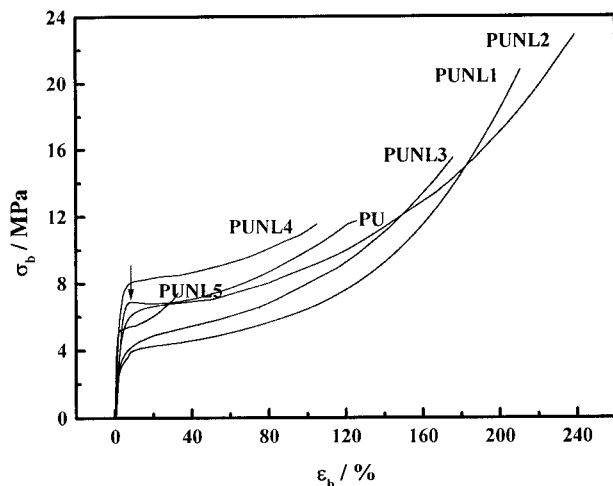


Figure 7 The strain–stress curves for PU and PUNL films cured at 20°C.

content but was lower than that of PU film, indicating that the flexibility arose from the networks formation between PU and NL chains as long as the additional NL was below 8%. However, when NL content was more than 8%, the crosslink densities of PUNL4 and PUNL5 films were lower than that of PU. It can be explained that when the NL content was more than 8%, phase separation occurred in the PUNL system, making the network formation via crosslinking more difficult. This is at variance with PU–nitrocellulose semi-IPNs, in which the breaking elongation decreased with an increase of nitrocellulose, and the crosslink density was much lower than that of PU, due to the absence of the crosslink networks

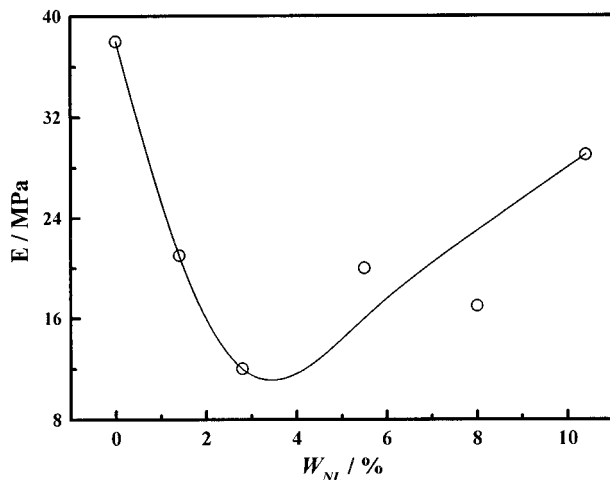


Figure 8 Effect of NL content (W_{NL}) on Young's modulus (E) for PU and PUNL films cured at 35°C.

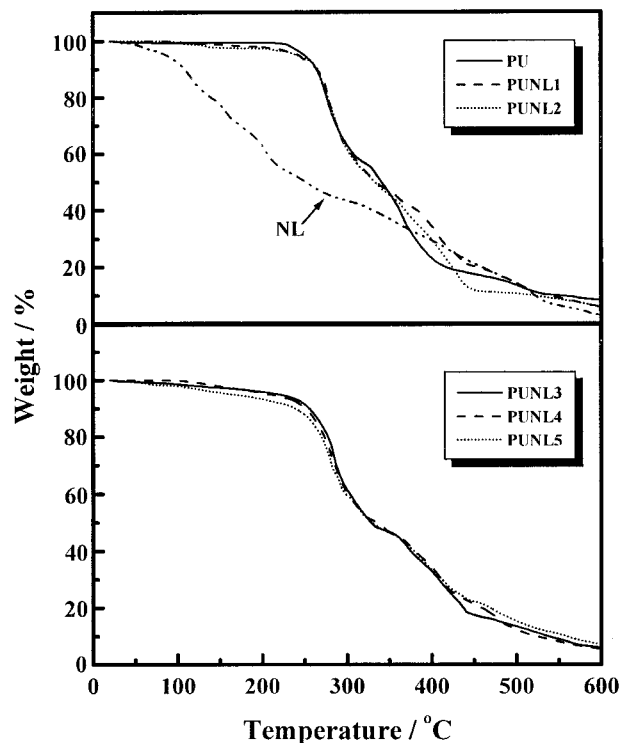


Figure 9 TGA curves as a function of temperature for PU, PUNL films, and NL.

of two kind of polymers.¹⁸ Therefore, the reacting power of NL with PU was higher than that of nitrocellulose.

Effect of NL Content on Thermal Properties

The TGA curves of PU, PUNL films, and NL are shown in Figure 9. The weight of NL gradually decreased with an increase in temperature. PU can be stable up to 215°C, then it decomposes in three distinct stages. PU was decrosslinked between 215°C and 325°C, which may be caused mainly by the breaking of urethane bond. This stage corresponds to about a 48% weight loss, which is approximately the amount of TDI and 1,4-butanediol incorporated into the PU. The second decomposition stage, in the temperature range of about 325°C to 436°C, was due to castor oil molecules and resulted in a faster rate of weight loss. From 436°C to 600°C, weight loss up to above 90% occurred because of unzipping of the molecular chains. The decomposition process of PUNL films was similar to that of PU. The effects of NL content on thermal stability of PU and PUNL films are listed in Table I. It is obvious that the PUNL films exhibited a slightly higher ther-

Table I Decomposition Temperature of PU and PUNL Films by TGA

Sample No.		PU	PUNL1	PUNL2	PUNL3	PUNL4	PUNL5
Decomposition	T_{d1} (°C)	252	262	262	260	260	262
Temperature	T_{d2} (°C)	325	363	365	361	360	358

mal stability than the PU film, which is attributed to covalent bonding between PU and NL.

CONCLUSION

A nitrolignin with $M_w = 20.6 \times 10^4$ can easily react with PU to form the crosslink networks. Polyurethane–nitrolignin (PUNL), a new network polymer, was satisfactorily synthesized from castor oil based–polyurethane and nitrolignin (NL) with a content of about 1.4–6%. Interestingly, both the tensile strength and breaking elongation of PUNL films with 1.4~6% NL content were much higher than those of PU film, and both tensile strength and breaking elongation of PUNL2 film with 2.8% NL content were 2 times higher than that of PU film. A suitable content of NL in PUNL films plays an important role in the promotion of PU network formation, resulting in the enhancement of crosslink density, whose contribution effectively enhances strength and toughness. Compared with the effects of nitrocellulose on PU, NL has a higher reactivity with PU. Therefore, moderate NL favors network formation rather than hindering the formation of a PU network.

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