

Structure and Properties of Semiinterpenetrating Polymer Networks Based on Polyurethane and Nitrochitosan

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ABSTRACT: Two semiinterpenetrating polymer networks (semi-IPNs) based on trihydroxyl methylpropane-polyurethane (T-PU) or castor oil-polyurethane (C-PU) were prepared by curing the mixed solution of the polyurethane prepolymer and nitrochitosan (NCH). During the curing process, crosslinking and grafting reaction between the molecules of the PU prepolymer and NCH occurred, because of the high reactivity of remaining hydroxyl groups in the NCH with —NCO groups of PU. The structure of the original semi-IPN sheets and the sheets treated with acetone were studied by infrared, ^{13}C -NMR, scanning electron microscopy, and dynamic mechanical analysis, showing interpenetration of NCH molecules into the PU networks. When nitrochitosan content (C_{NCH}) was lower than 10 wt %, the semi-IPN sheets T-PU and C-PU had higher density and tensile strength (σ_b) than the systems with C_{NCH} more than 20%. The trihydroxymethyl propane-based PU reacted more readily with nitrochitosan to form the semi-IPNs than castor oil-based PU. The semi-IPN coatings T-PU and C-PU were used to coat cellophane, resulting in intimate interfacial bonding. The mechanical strength and water resistivity of the cellophane coated with T-PU coating were improved remarkably. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3109–3117, 2001

Key words: semiinterpenetrating polymer networks; polyurethane; nitrochitosan; chitosan; cellulose film

INTRODUCTION

Interpenetrating polymer networks (IPNs) constitute a rapidly developing branch of polymer composite materials, which may combine the properties of the components forming networks.¹ The IPNs, composed with polyurethane (PU) as a component, are the most prospective and applicable ones, because the polyurethane prepolymer

readily mixes with other monomers or prepolymers, and they reacted in parallel without interference to form IPN materials with excellent properties. Furthermore, it can be controlled in terms of processing and composition to meet a vast variety of product requirements. Suggested applications of IPNs include use as damping materials,^{2–4} biomedical materials,^{4,5} gas transport membranes,^{6,7} electrical/electronic devices,⁸ and coating materials.^{9–11} A cured PU/poly(methacrylate-co-styrene) coating was a semi-IPN,⁹ where only one of the polymers was crosslinked.¹² Thermodynamic incompatibility between two polymers, by permanently interlocking network segments and IPNs with limited phase separation, could be obtained.^{1,13} As a rule, IPNs are microheterogeneous systems because of the incompatibility between components that causes

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microphase separation. The homogeneity can be achieved by choosing a kinetic regime in such a way that crosslinking occurs faster than microphase separation.¹⁴

Recently, the utilization of renewable resources has become of increasing interest because of their potential to substitute for petrochemicals. Chitin is one of the more abundant natural raw materials. Its deacetylated product, chitosan, can be readily dissolved in dilute acids, and has found some industrial applications. In our laboratory, the grafted, semi- and full-IPNs coatings from PU with natural products, such as depolymerized chitosan, nitrocellulose, nitrolignin, and elaeostearin, have been satisfactorily synthesized, exhibiting excellent mechanical properties and biodegradability.^{9-11,15,16} Chitosan itself was used as one component of semi-IPN coating.¹¹ It is worth noting that the IPN coatings synthesized from castor oil-based PU with chitosan, nitrocellulose, or elaeostearin were decomposed into small molecules by micro-organisms in soil,¹⁷ suggesting that the IPN coating of PU/chitosan should be biodegradable. Castor oil is also one of the natural polyols, and most useful for the synthesis of polyurethane crosslinking networks in IPNs, due to its three reactive hydroxyl groups.

This article concerns the synthesis and characterization of novel semi-IPNs, which were made from PU and nitrochitosan. Their structure, compatibility, and densities were measured by infrared (IR), ¹³C NMR, dynamical mechanical analysis (DMA), and scanning electron microscopy (SEM). The ultimate properties as coating to cellophane were investigated.

EXPERIMENTAL

Materials

Chitosan was supplied by Zhejiang Yuhuan Sea biochemical Co., and used without further purification. The degree of the deacetylation was determined to be about 87% by ¹H-NMR. Its weight-average molecular weight (M_w) was measured to be ca. 3.5×10^5 by a DAWN-DSP multiangle laser photometer (Wyatt Technology Co.) combined with a P 100 pump (Thermo Separation Products), equipped with a TSK-GEL G4000 HHR column (7.8×300 mm) at the flow rate of 1.0 mL/min with tetrahydrofuran (THF) eluent at 25°C.

Trihydroxymethyl propane (TMP) and castor oil were chemical grade, and dehydrated at 100°C

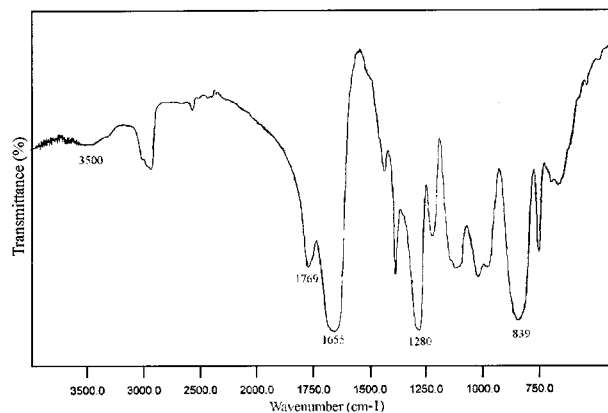


Figure 1 FTIR spectrum of nitrochitosan.

under 20 mmHg for 10 h before use. 1,4-Butyldiol (BTO) was treated with 3 Å molecular sieves overnight, and then distilled. 2,4-Tolylene diisocyanate (TDI) was redistilled before use. Ethyl acetate, cyclohexane, aceticanhydride, and nitrosonic acid were analytic grade.

Preparation of Nitrochitosan

The nitrochitosan (NCH) was prepared according to the following procedure. One gram of chitosan was added slowly to 150 mL of nitrosonic acid, which was cooled using an ice/salt bath, then 100 mL of aceticanhydride was introduced in droplet under vigorous stirring. Four hours later, the mixture was poured into ice water to end the reaction. The precipitate was collected and washed thoroughly with distilled water and then with ethanol twice. It was purified by redissolving in acetone, and filtered to remove the insoluble part. After evaporating the solvent under pressure, it was vacuum dried at room temperature for 10 h to obtain a white powder product. Its weight-average molecular weight (M_w) was measured by light scattering, as mentioned above to be 1.85×10^5 . The FTIR spectrum of the resulting nitrochitosan (Fig. 1) showed absorption at 1725 cm^{-1} ($\nu_{\text{N=O}}$), 1638 cm^{-1} ($\nu_{\text{O-NO}_2}$), and 1281 cm^{-1} ($\nu_{\text{N-O}}$), and the intensity at 3500 cm^{-1} was decreased sharply, resulting from the substitution of the —OH and —NH₂ groups with the —NO₂ group. The ¹³C-NMR spectrum of NCH was recorded on a Varian Mercury 300 spectrometer in acetone-d₆ at 50°C. Figure 2 shows the ¹³C-NMR spectrum of nitrochitosan in deuterated acetone (CD₃COCD₃) at 50°C. Comparing with the spectrum of chitosan,¹⁸ the peaks were designated as C1 (106.5 and 100.5 ppm), C3, C4, C5, C6

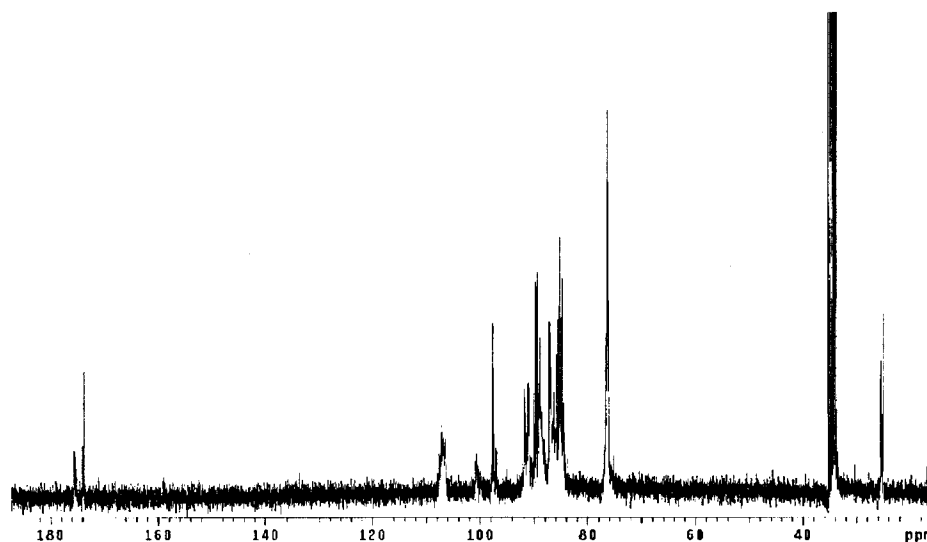


Figure 2 ^{13}C -NMR spectrum of nitrochitosan in acetone- d_6 at 50°C .

(84–98 ppm), C2 (76 ppm), and —C=O (174.5 and 174.8 ppm). The substitution of the —NO_2 group resulted in the split of the peak of C=O and C1 into two peaks, respectively. The nonselective nitro-substitution of the chitosan occurred at the C2, C3, and C6 positions.

Preparation of PU/NCH IPNs

To a three-necked round-bottom flask equipped with mechanical stirring and N_2 inlet, 13.4 g (0.1 mol) of TMP and 68 g of cyclohexane were added. Following completely dissolution, 52.25 g (0.3 mol) of TDI was introduced in droplets. The reaction was stopped after reaction for 5 h at 80°C . The PU prepolymer obtained was kept in a desiccator and coded as T-PU. The PU prepolymer coded as C-PU was prepared with the same procedure stated above, but the reagents were 50 g (0.054 mol) of castor oil and 42 g (0.024 mol) of TDI. The theoretical ratio of NCO : OH of PU prepolymer was 2 : 1.

Two grams of PU prepolymer, 0.09 g of BTO as a chain extender, and a stoichiometric amount of nitrochitosan were mixed in 11 g of ethyl acetate. The mixture was stirred at room temperature for 1 h, and then poured into a Teflon trough, with the size of $18 \times 10 \times 0.5 \text{ cm}^3$. It was cured at 60°C for 10 h. The sheets obtained with nitrochitosan contents of 0, 5, 10, 20, and 30% (wt %) were coded as T-PU0, T-PU5, T-PU10, T-PU20, and T-PU30, respectively. Sheets coded as C-PU0, C-PU5, C-PU10, C-PU20, and C-PU30 were prepared from the C-PU prepolymer in the same manner.

To study the interaction between PU and NCH, soxhlet extractions were carried out using acetone as solvent for 10 h, and then the sheets were vacuum dried at 60°C for 10 h. The extracted semi-IPN sheets were coded as T-PU0-2, T-PU5-2, T-PU10-2, T-PU20-2, T-PU30-2, and C-PU0-2, C-PU5-2, C-PU10-2, C-PU20-2, and C-PU30-2, respectively.

Cellophane Coated with PU/NCH

Commercial cellophane was supplied by Hubei Chemical Fiber Manufacture in China. The coatings T-PU and C-PU were diluted by ethyl acetate to give 10% solids content, and then coated on both sides of the cellophane, respectively. The coated films were cured at 80°C for 30–150 min. The coating amount on cellophane (2.4 mg cm^{-2}) was 0.4 mg cm^{-2} ; therefore, the coating layers in the coated film accounted for 14%, suggesting a coating layer $1.5 \mu\text{m}$ deep for each side. The coated films obtained were coded as films T-PU/RC, with T-PU coating, and C-PU/RC with C-PU.

Characterizations

The density (ρ) of the IPN sheets was measured by determining the weight of a volume-calibrated psychomotor filled with a mixture of ZnCl_2 aqueous solution and distilled water, in which the samples achieved floatation level. The density of the liquid mixture equals the density of the samples. Three parallel measurements were carried out for every sample. The density of both the

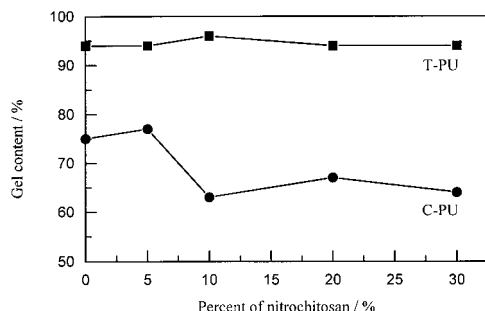


Figure 3 Dependence of gel content for semi-IPN sheets on nitrochitosan content.

original sheets and extracted sheets was measured. Gel contents in the sheets were calculated from dry sheets before and after extraction.

Infrared spectra were measured using a KBr plate on an FTIR 8000 series Testscan (Shimadzu). Dynamic mechanical analysis were carried out with a Netzsch DMA 242 viscoelastometer in a temperature range of -110 – 200°C , a frequency of 16.6 Hz, and a heating rate of $5^{\circ}\text{C}/\text{min}$.

The morphology of the surface and cross-section of the semi-IPN sheets was observed by scanning electron microscopy (SEM, Hitachi S-570). The sheets were fractured in liquid nitrogen to preserve the cross-section, and then sputter-coated with gold prior to being viewed under the microscope.

The mechanical properties were measured on a universal testing machine (CMT6503, Shenzhen SANS Co., Ltd) at ambient temperature. The test procedure followed the ISO6239-1986 standard with a tensile rate of 5 mm/min. Mean value of five parallel measurements per sample was recorded. The water resistivity (R) of the coated films was obtained according to the previous method.⁹

EPMA was done by using an Electron Probe Microanalyser JXA-8800R (JEOL Super-Probe, Japan). The elector-conductive film was fixed between two steel sheets. The one- and two-dimensional distributions of nitrogen on the film were analyzed by an electron probe X-ray energy spectrograph.

RESULTS AND DISCUSSION

Dependence of gel content on percent of nitrochitosan for the two semi-IPN sheets is illustrated in Figure 3. The gel content of all T-PU IPN sheets is

about 95%, indicating that most of the nitrochitosan in the PU networks cannot be redissolved by warm acetone. However, the gel content was less than 80% for the C-PU sheets, and decreased with an increase of the nitrochitosan content, indicating a relatively weak interaction between NCH and PU in the C-PU.

The composition dependence of the density of the IPN system is shown in Figure 4. In a polymer blend, where there is adhesion between the interface and no molecular mixing at the phase boundary, the density of the blend would be expected to follow the rule of mixtures. The compatibility of the IPN system depends on the composition of the two polymers. T-PU sheets possess higher densities than that given by the rule of mixtures up to 10 wt % NCH. After extraction, the densities of the sheets were lower than that of the original one, resulting from the removal of NCH in the semi-IPNs by dissolving in acetone. Interestingly, the densities of the T-PU-2 series show positive deviation. The T-PU5-2 sheet, with NCH content of 5%, especially shows the largest positive deviation, indicating that strong interaction took place between these two components in the sheet T-PU2. It may be caused by a graft reaction be-

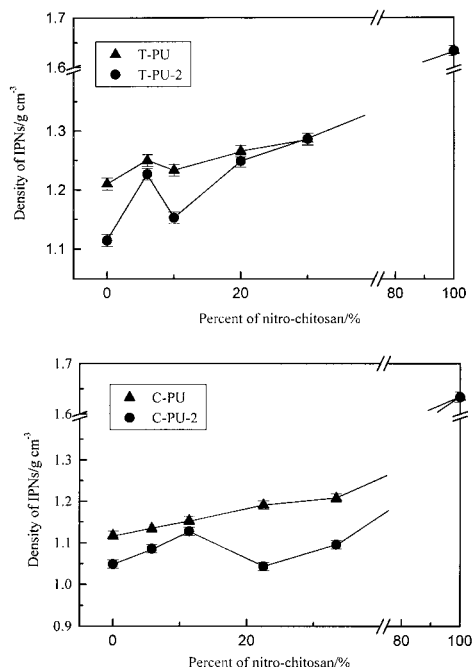


Figure 4 (A) Plots of density of the sheets against percent of nitrochitosan T-PU and T-PU-2 represent original and extracted sample. (B) Plots of density of the sheet against percent of nitrochitosan C-PU and C-PU-2 represent original one and extracted sample.

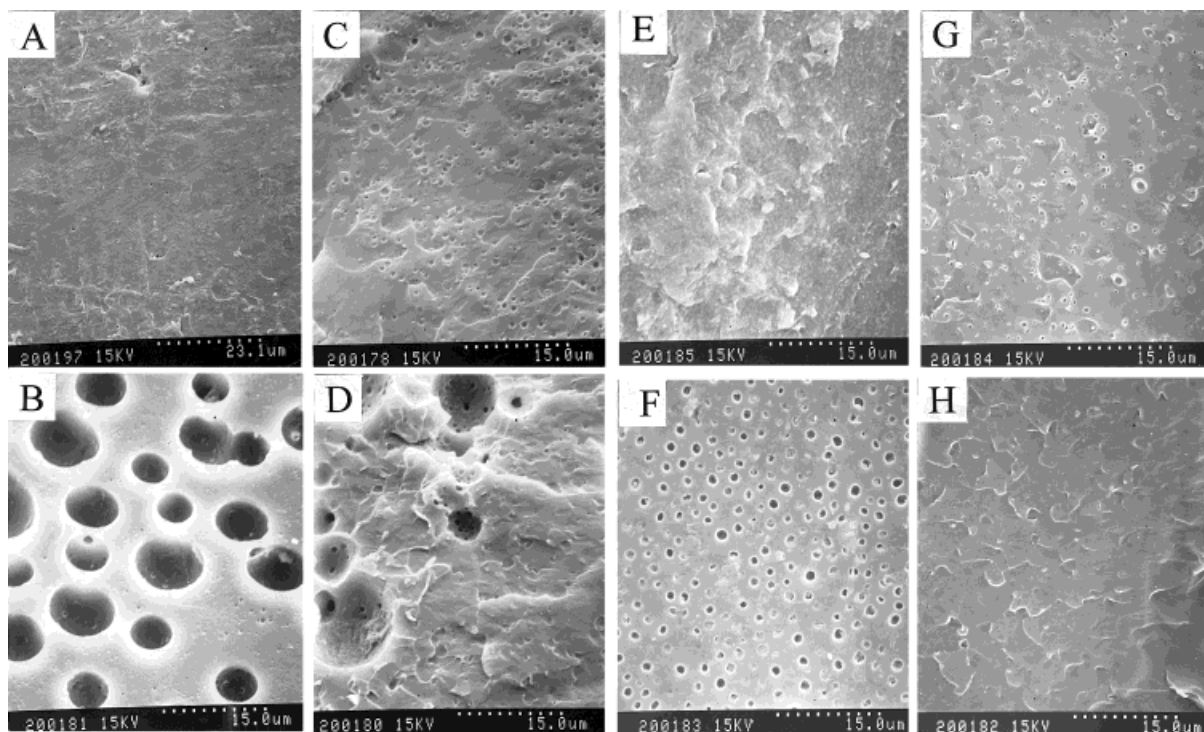


Figure 5 SEM photographs of the coating sheets: C-PU10S (A) and C-PU20S (E) for original surface; C-PU10C (C) and C-PU20C (G) for original section; C-PU10-2S (B) and C-PU20-2S (F) for surface after extraction; C-PU10-2C (D) and C-PU20-2C (H) for section after extraction.

cause the remaining active hydrogen atom can react with the —NCO groups of the T-PU network. For the C-PU system, negative deviation of the densities was observed over the whole experimental range. Even after extraction, no obvious positive deviation was observed for the densities of the C-PU-2 series. Its densities deviated largely from the rule of mixtures for semi-IPN sheets with NCH content higher than 20%, suggesting that the compatibility of the two components C-PU and NCH decreased with increase of NCH content. Concerning the difference between the two semi-IPN systems, it can be explained that the monomer TMP with low molecular weight and short chain may be more easily reacted with TDI to form a network for the T-PU system than castor oil for C-PU. The molecular chain of castor oil is relatively long, resulting in steric hindrance of the crosslinking.

Figure 5 shows SEM photographs of the surface and cross-section of the sheets C-PU10 and C-PU20. After extraction, holes are observed on the surface, and the hole size of C-PU20 with 20% NCH is much larger than that of C-PU10 with 10% NCH. Furthermore, the cross-section struc-

ture of both the original and extracted C-PU10 was denser than that of the surface. This indicated that the NCH part was extracted more readily to form holes on the surface than internally in the sheets. The results supported the conclusion from Figure 4.

Figure 6 shows the DMA spectra of the semi-IPN sheets. An unsymmetrical peak spectrum, corresponding to the peak temperature at 59.6°C , was observed for the original sheet C-PU10. However, a shoulder and a broad peak (59.6 and 75°C)

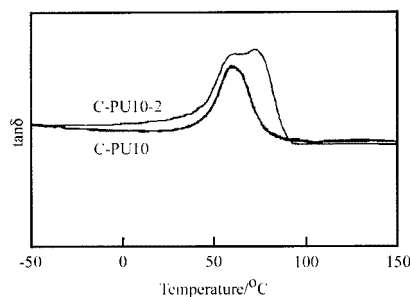


Figure 6 DMA spectra of the coatings C-PU10 (original) and C-PU10-2 (after extraction).

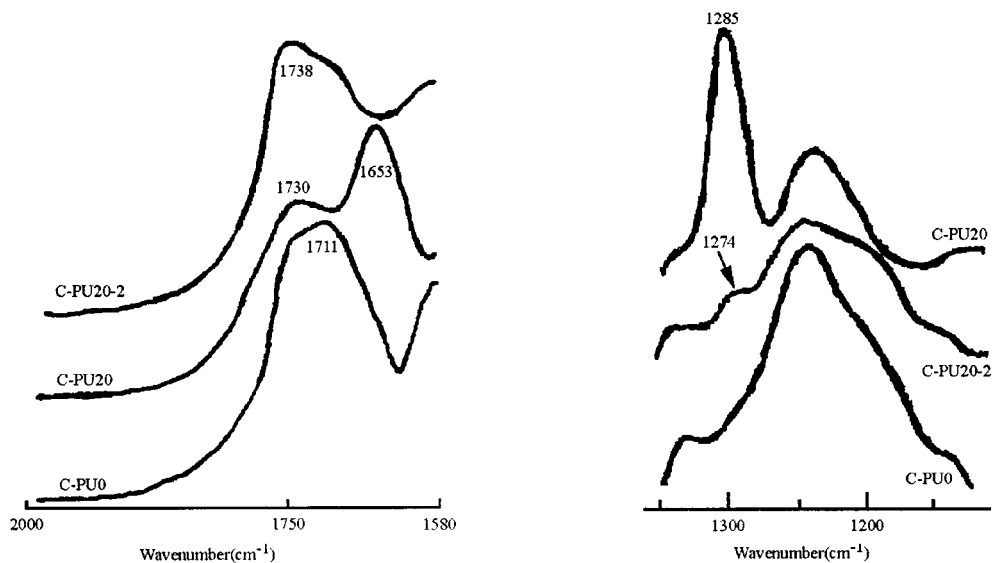


Figure 7 FTIR spectra in the carbonyl and nitril stretching frequency region of the original films C-PU0, C-PU20, and extracted film C-PU20-2.

appeared for the extracted C-PU10-2. The peak temperatures related to the glass transition temperature of the PU network. This indicated that two kinds of PU networks exist in the sheet, namely two T_g s. This can be explained by a reaction of some NCH with part of the PU networks occurring during extraction and drying, resulting in grafted IPNs with relative high T_g in the sheet C-PU10-2. The explanation was supported by the results from IR. Figure 7 shows the FTIR spectra in the carbonyl and nitril stretching frequency region of the sheet C-PU. In the nitril stretching frequency region, two characteristic absorbances at 1653 and 1285 cm^{-1} for NCH in IPN C-PU20 appeared. After extraction, the two peaks disappeared, and a shoulder peak appeared at 1274 cm^{-1} . These results suggest that the free nitril groups in the PU network reacted with NCH in the course of extraction and drying, leading to a lower shift for the nitril stretching frequency. In the carbonyl region of 1711–1738 cm^{-1} , the absorbance and shape of the peak changed remarkably for extracted sheets, compared with the original one. Therefore, for complete formation of the semi-IPNs from C-PU with NCH more time at 60°C is needed.

Figure 8 shows the dependence of tensile strength (σ_b) on the nitrochitosan content of the sheets. The σ_b of the C-PU series increased linearly with the increase of the NCH content up to 10%, then decreased with increasing NCH content. For the T-PU series, the σ_b increased

slightly when the NCH content decreased lower than 5%. The strength of the T-PU sheets was clearly higher than that of C-PU, owing to enhancement in interpenetrating and entanglement between molecules of T-PU and NCH. As stated above, the relatively low mechanical properties of the sheet C-PU are due to incomplete formation of semi-IPNs.

The T-PU5 and C-PU10 showed better mechanical properties, so they were used to coat the cellophane to obtain water-resistant cellulose film. The light transmittance of the coated films was 90% at 600 nm, the same as that of cellophane. Usually, the interface between two materials will cause losses in optical transmission because of the quantity of light, which is normally scattered and reflected at the interface of different solid materials. The excellent light transmit-

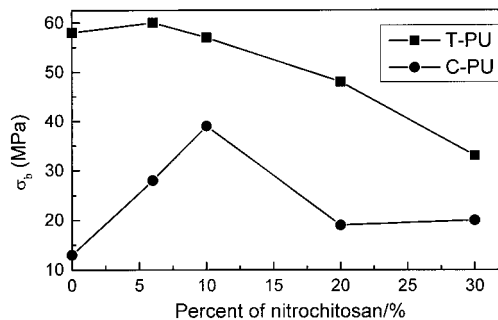


Figure 8 Plots of tensile strength (σ_b) against percent of nitrochitosan for the sheets T-PU and C-PU.

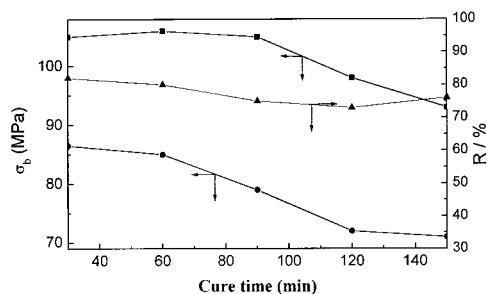


Figure 9 Plots of tensile strength (σ_b) and water resistivity (R, \blacktriangle) against cure time at 80°C for the film T-PU/RC in dry (\blacksquare) and wet (\bullet).

tance of the coated film resulted from the strong interfacial bonding between the cellulose and the semi-IPN coating T-PU5 or C-PU10. Figures 9 and 10 show tensile strength (σ_b) and water resistivity (R) against cure time at 80°C for the coated films T-PU/RC and C-PU/RC, respectively. The tensile strength and water resistivity of the coating sheets, coated cellophane films, and cellophane are summarized in Table I. Obviously, the σ_b values of the coated cellophane films T-PU/RC and C-PU/RC were larger than that of the cellophane (RC film) in dry and wet states, when the cure time was 60 min for T-PU/RC and 90 min for C-PU/RC. The water resistivity of both T-PU/RC and C-PU/RC are much larger than that of RC film. Interestingly, the σ_b values for coated films were all more than that of both the coating sheet and RC film, suggesting a strong interaction between the coating layer and the RC film.

The one-dimensional distribution (A) and the photographs of the two-dimensional distributions (B) in the cross-section for the coated films T-PU/RC and C-PU/RC, analyzed by electron probe X-ray energy spectrographs, are shown in Figure 11. For the right figures marked as NK, the ni-

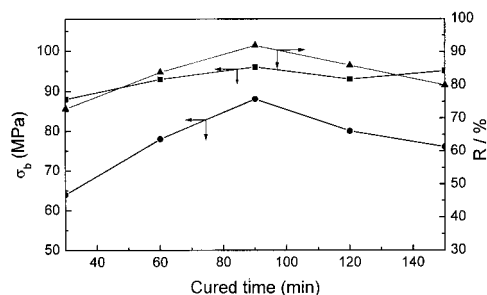


Figure 10 Plots of tensile strength (σ_b) and water resistivity (R, \blacktriangle) against cure time at 80°C for the film C-PU/RC in dry (\blacksquare) and wet (\bullet).

Table I Tensile Strength (σ_b)^a and Water Resistivity (R) of Coating Sheets, Coated Cellulose Films, and Cellophane

Sample	σ_b (MPa)		R (%)
	Dry	Wet	
T-PU 5	60		
C-PU 10	39		
T-PU/RC 2	106	86	81
C-PU/RC 3	96	88	92
Cellophane	94	50	53

^a Error margins were $\pm 5\%$.

trogen content of PU was detected not only in the coating layer but also in the RC film, and the distribution of nitrogen was almost the same from the surface to the middle for coated film C-PU/RC, similar to RC film coated with PU.¹⁹ However, the distribution of nitrogen for the coated film T-PU/RC decreased gradually from two sides to the middle. Concerning the difference between the two coated films, it was regarded that T-PU coating could be cured as fast as 10 min at 80°C, but the C-PU coating took at least 24 h to be cured to the same condition, to leave enough time to allow the PU prepolymer molecules to diffuse into the RC film. The left figures, marked as SE, are secondary electron images. The bright band on both sides of the film are protuberances of the surface layers, and reflect a more fixed structure by the penetrating coating than that in the middle, where the concave structure is attributed to the cellulose film contraction. Analysis of the EPMA results indicates that the PU prepolymer penetrated into the RC film to form a shared PU network crosslinked with the semi-IPN coating and cellulose.⁹ The coating based on T-PU with nitrochitosan more readily formed semi-IPNs than did C-PU.

CONCLUSIONS

Two semiinterpenetrating polymer networks coatings from trihydroxymethyl propane-based PU/nitrochitosan (T-PU/NCH) and castor oil-based PU/nitrochitosan (C-PU/NCH) were prepared, respectively. Most of the nitrochitosan in the network cannot be redissolved by warm acetone, suggesting that a grafting reaction of some NCH with part of the PU in the semi-IPN sheet

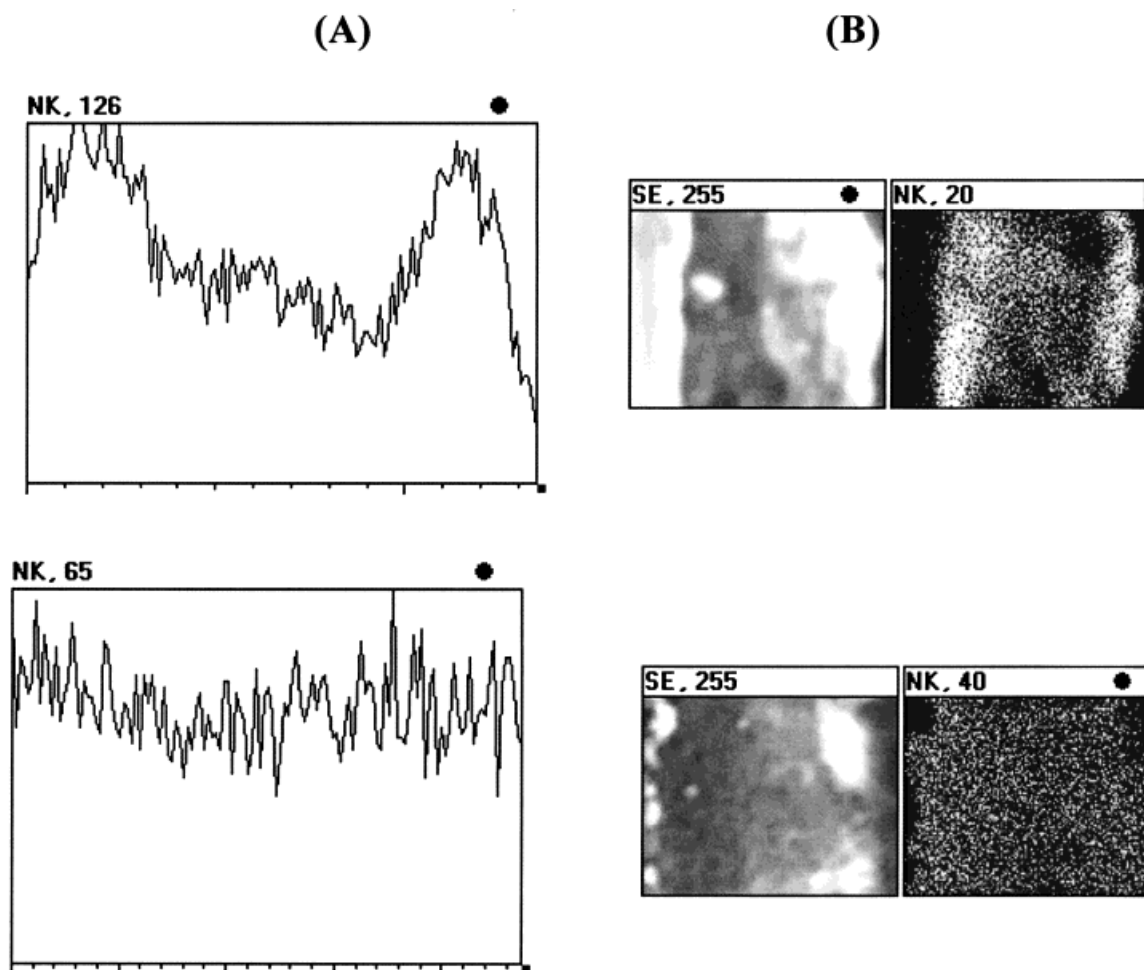


Figure 11 EPMA on the cross-section of the T-PU/RC film (top) and C-PU/RC film (bottom) for the one-dimensional distributions (A) and the two-dimensional distributions (B); SE is marked as secondary electron images; N, nitrogen; K, K-alpha.

occurred. The semi-IPN coatings possess higher mechanical properties and densities than the original PU, when the nitrochitosan content was 5 and 10% in the IPN sheets T-PU and C-PU, respectively. The trihydroxymethyl propane-based PU more readily reacted with nitrochitosan to form networks than castor oil-based PU. As coating materials, both T-PU and C-PU have intimate interfacial bonding with cellophane, owing to the diffusion of PU prepolymer molecules into cellulose. The mechanical strength and water resistivity of the cellulose film coated with T-PU IPN were improved considerably.

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