

Synthesis and Characterization of Polyurethane–Chitosan Interpenetrating Polymer Networks

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ABSTRACT: A polyurethane–chitosan (PU–CH) coating was synthesized from castor-oil-based PU prepolymer and highly deacetylated and depolymerized chitosan. The films cast with the coating were used for the characterization. X-ray photoelectron spectroscopy, a surface-sensitive technique, indicated the chemical bonding between the chitosan and PU prepolymer as well as the enrichment of chitosan on the surface of the film PU–CH. Electron spin resonance (ESR) spectroscopy using the nitroxyl radical 4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl (4-hydroxy-TEMPO) as a reporter group was used to study the chain mobility in the film PU–CH. It was observed that T_{50G} of the probe and the first glass transition temperature (T_{g1}) of the film PU–CH were 10 and 18°C higher than those in the PU film, respectively, and the activation energy (27.0 kJ mol⁻¹) of tumbling for the probe covalently bonded with PU–CH was 12.8 kJ mol⁻¹ higher than that of the probe with the film PU. It suggests that the molecular motion in the PU–CH was restricted by grafted and crosslinked interpenetrating polymer networks (IPNs). The results of the differential thermal analysis and thermogravimetric analysis proved that the thermostability of the film PU–CH was significantly higher than that of the film PU, and the T_{g1} value is in good agreement with that calculated from ESR. It could be concluded that the IPNs resulted from the chitosan grafting and crosslinking with PU exist in the film PU–CH. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1321–1329, 1998

Key words: synthesis; polyurethane; chitosan; IPNs; castor oil; electron spin resonance

INTRODUCTION

The interpenetrating polymer networks (IPNs) provide a convenient route for modification of properties to meet specific needs. The IPNs based on poly(methyl methacrylate) (PMMA) and polyurethane (PU), which were prepared by reacting tolylene diisocyanate (TDI) with hydroxy-terminated polybutadiene (HTPB) in the presence of stannous-type catalyst, were reported for studying the effect of the composition on properties.¹ Recently, the utilization of renewable resources has become of increasing interest because of their

potential to substitute for petrochemical derivatives. For example, castor oil, an important commercial oil extracted from beans of the plant *Ricinus communis*, was used to produce a number of polyurethanes for IPNs.^{2,3} Moreover, chitin is also an abundant raw material from agricultural waste. The chitin is not soluble in most solvents, but its deacetylated product, chitosan, can be readily dissolved in acids and has found some industrial applications. It is worth noting that biodegradable PU block copolymers based on depolymerized cellulose derivatives, such as cellulose triacetate, have been prepared.^{4,5} It reminded us that the materials synthesized from castor-oil-based PU and chitosan, as well as its derivatives, should be biodegradable.

IPN and semi-IPN coatings are currently being

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investigated in our laboratory in order to improve the water resistivity of the regenerated cellulose (RC) films.^{6–9} However, when poly(methyl methacrylate-*co*-styrene) (PMMA-St), which could form IPNs to accelerate the cure of PU coating and to improve the mechanical properties,⁹ was added, the biodegradability of the RC films coated with PU/PMMA-*co*-St would be reduced. In this work, a depolymerized chitosan was used to substitute for PMMA-St in the coating mentioned above, hoping that polyurethane/chitosan (PU-CH) coating can not only be cured speedily but also improve the mechanical properties and the biodegradability.

In the field of polymer characterization, X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR) spectroscopy were used to investigate the surface structure and the molecular motion of polymers, respectively. XPS is a surface-sensitive technique. Using this method, Ratner¹⁰ and Paik Sung and Hu¹¹ discovered that the soft segments were enriched on the surface of the segmented PU films. The chain mobility in the bulks of polymers can be detected by ESR spectra of paramagnetic probes, which are usually stable nitroxyl radicals embedded in polymers matrices. The advantage of ESR is that no other signals are superimposed on the ESR signals because only paramagnetic species are detected. The spin probe technique was employed to study the interactions between organic nitroxides and host polymers by Rabold.¹² From then on, the polymer transitions, molecular motions and segmental size of vulcanized natural rubbers, modified PU blends, and random ionomers have been investigated by ESR.^{13–16} According to this method, two important parameters are used to characterize the motion of probe molecules. One is the temperature at which the extrema outer line separation (ΔW) is 50 Gauss, or T_{50G} , which depends on the structures of both the radical and the polymer. The other is the tumbling activation energy of the probe, which is tightly correlated to the chain mobility of the host polymers, especially when the probe molecules are covalently bonded with the polymers.

EXPERIMENTAL

Materials

All the reagents except for the probe were purchased from commercial resources in China.

Caster oil, chemical pure, was dehydrated at 100°C under 20 mm Hg for 1 h. 2,4-Tolylene diisocyanate (TDI) was redistilled before use. Ethyl acetate was analytical grade. The chitin was supplied by Tianbao Chitosan Ltd. Co. of Zhejiang province in China. 4-Hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl (4-hydroxy-TEMPO) was purchased from SIGMA Chemical Co., and used for the spin probe.

Synthesis of PU-CH

Highly deacetylated chitosan was prepared according to the Mima et al.¹⁷ The chitin was treated alternately by dilute acid and concentrated sodium hydroxide solutions for 5 times to get the chitosan. Then, in order to depolymerize and further improve the degree of deacetylation (DD) of the chitosan, 10% H₂O₂ aqueous solution was added to the chitosan and stirred at 80°C for 2 h. The infrared (IR) spectra of the chitosan for both before and after the depolymerization were recorded with Nicolet 650 Fourier transform infrared (FTIR) spectrometer and are shown in Figure 1. Before the depolymerization of the chitosan, the bands at 1650 and 1705 cm⁻¹ (region I) exist in the IR spectra, which were assigned to the residue of —NHCOCH₃, and a broad and strong band at 2860–3500 cm⁻¹ (region II), which were assigned to the H-bonded —OH and —NH₂ groups. After the depolymerization, the absorption in region I almost disappeared completely, and the bands in the region II became sharp and narrow, which were resulted from the crystallization of the chitosan due to the higher deacetylation.¹⁷ The DD of the chitosan could be evaluated¹⁸ to be 80 and 98%, respectively, for before and after the depolymerization.

According to the Mark-Houwink equations for chitosan with different DD,¹⁹

$$[\eta] = 1.42 \times 10^{-3} M^{0.94} \quad (\text{for } 80\% \text{ DD}) \quad (1)$$

$$[\eta] = 16.8 \times 10^{-3} M^{0.81} \quad (\text{for } 98\% \text{ DD}) \quad (2)$$

the viscosity-average molecular weights (M_η) of the chitosan were measured by using viscometry and found to be 27,400 and 6500 for before and after the depolymerization, respectively. This highly deacetylated and depolymerized chitosan was used in this work.

A three-necked flask was fitted with a nitrogen inlet tube, stirrer, and pressure-equalizing dropping funnel. 5.0 g of chitosan dissolved in 5.0 mL

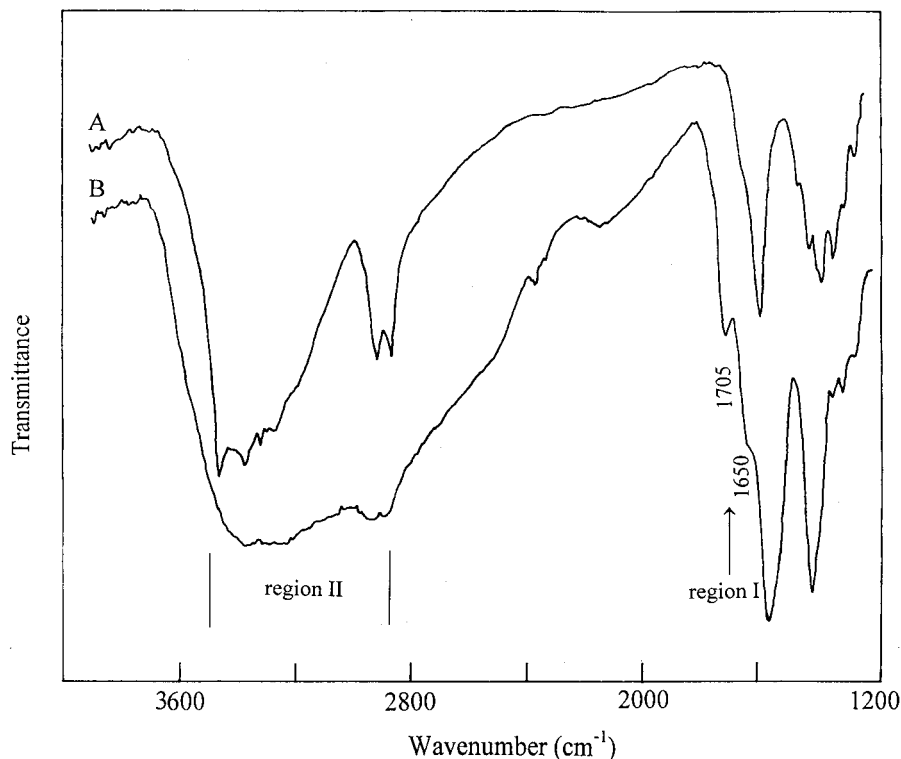


Figure 1 IR spectra of chitosan (A) after and (B) before deacetylation.

of glacial acetic acid was mixed with 42.0 g of castor oil and then poured into the dropping funnel. 24.0 g of TDI was introduced in the flask at 20°C, and then the mixture of chitosan-castor oil was added with the stirring under nitrogen atmosphere. The dropping was completed within 20 min, then stirring was continued for 40 min to get the PU-CH prepolymer. The viscosity of the PU-CH prepolymer was measured with a rotary viscometer and was given to be 3.6×10^4 mPa s. The PU was prepared in the way described in a previous work.⁹ The ratio between castor oil and TDI (castor oil/TDI) was 10.0 : 5.0 by weight. After reacting at 40°C for 1 h, the viscosity of the PU prepolymer was measured to be 1.5×10^3 mPa s.

The PU-CH prepolymer was dissolved in ethyl acetate (EA) (solid content 20%), then the coating solution was cast on a clean glass plate to form a film and cured at 90°C for 20 min. The plate stayed at room temperature for 24 h, and the film PU-CH with approximately 40 μm thickness was obtained. The film PU was prepared in the same way except for a longer cure time (>40 min).

Characterization

The elemental compositions of the films PU-CH and PU were measured by using a MOD 1106

elemental analyzer (CARLO Erba Strumentazione, Italy). The thermal differential analysis (TDA) and thermogravimetric analysis (TGA) of the films were performed simultaneously by using a PRT-2 thermal analyzer (Beijing Optical Instrument Factory, China) under 40 mL/min N_2 flow at the heating rate of 10 mv/h. XPS spectra of the films were recorded on a KRATOS XSAM 800 XPS spectrometer. The vacuum system was kept below 1.33×10^{-6} Pa. A magnesium anode producing $\text{MgK}\alpha$ X-rays at 1253.6 eV was used as the X-ray source. The binding energies were referenced to unfunctionalized carbon at 285.00 eV. The emission angle of electrons was set at 90°, which resulted in an information depth of about 5 nm.

ESR measurements were made on a JES-FEIXG ESR spectrometer (JEOL, Japan) operating in the X-band. Spectra were recorded using the following instrumental parameters: sweep width, 3300 ± 250 G; modulation frequency, 100 KHz; modulation amplitude, 2 G; microwave power, 1 mW; time constant, 30 ms. 4-Hydroxy-TEMPO was used as the probe. The probe solution was made by dissolving 1 mg of 4-hydroxy-TEMPO in 100 ml of EA. The concentration of the probe in the sample film was controlled less than 5×10^{-4} by weight. The PU-CH and PU prepolymers were

Table I Elemental Analysis Results of PU-CH and PU Films

	PU-CH			PU		
	C	N	H	C	N	H
Theoretical (%)	65.73	5.65	10.47	69.62	5.36	8.59
Experimental (%)	68.29	5.73	8.92	68.34	5.32	8.64

dissolved in EA to reach solid content 20%, then cured at 90°C for 20 min (for PU-CH) and more than 40 min (for PU), respectively. Eventually, the films of 40 μm thickness were cut into 5.0 \times 0.2 cm^2 size for use.

RESULTS AND DISCUSSION

The elemental analysis results of the films PU-CH and PU are listed in Table I. According to the composition used in sample preparation, the N element content in the film PU-CH should be higher than that in PU, as indicated by the theoretical values given in the table. The experimental results turned out to be in good agreement with the theoretical prediction, suggesting that no chitosan loss occurred during the preparation of the film PU-CH.

Figure 2 shows the two N_{1s} spectra (the binding energy of N_{1s} electrons) of the films PU-CH and PU from XPS analysis. Both curves were roughly symmetrical and sharp, suggesting that the N element was in one state or more than one but very similar states. The binding energy of N_{1s} for the film PU-CH was 399.98 eV while that for the film PU appeared at 400.24 eV. This could be related to the reaction of chitosan $-\text{NH}_2$ groups of chitosan with $-\text{NCO}$ groups of PU prepolymer. It was thought that there were two states of the N element in the film PU-CH, namely $\text{NHCONH}-$ (state I) and $-\text{NHCOO}-$ (state II). Because the binding energy of N_{1s} in state I was slightly lower than that in state II,^{10,11} the apparent value of N_{1s} for the film PU-CH was 0.26 eV lower than that for the PU film. Figure 3 shows C_{1s} spectra of the films PU-CH and PU. The two spectra show similar shape and binding energy. The C_{1s} spectrum of the film PU-CH consisted of two peaks. The peak at 285.00 eV was assigned to C-C (C-H) bonds, and the other at 289.10 eV to the combined contributions of $-\text{NHCONH}-$ and $-\text{NHCOO}-$ groups. For the PU film, the two consisting peaks of C_{1s} spectra were located at

285.00 and 289.24, respectively. It is indicated that there was only one type of carbonyl groups in PU film and ester carbonyl groups have higher C_{1s} binding energy than urea carbonyl groups in the film PU-CH. These results implied that chemical bonds exist between chitosan and the PU prepolymer.

In the XPS spectra, the strength ratio of C_{1s} between the films PU-CH and PU ($C_{1s,\text{PU-CH}}/C_{1s,\text{PU}}$) was 0.90 and $N_{1s,\text{PU-CH}}/N_{1s,\text{PU}}$ was 0.71. It was reported^{10,11} that certain PU soft segments enriched on the surface of the film PU. The chitosan in the film PU-CH is a special soft segments. From the above data about the binding energy, chemical states, and the N_{1s} and C_{1s} strength ratios, it could be assumed that the chitosan unit

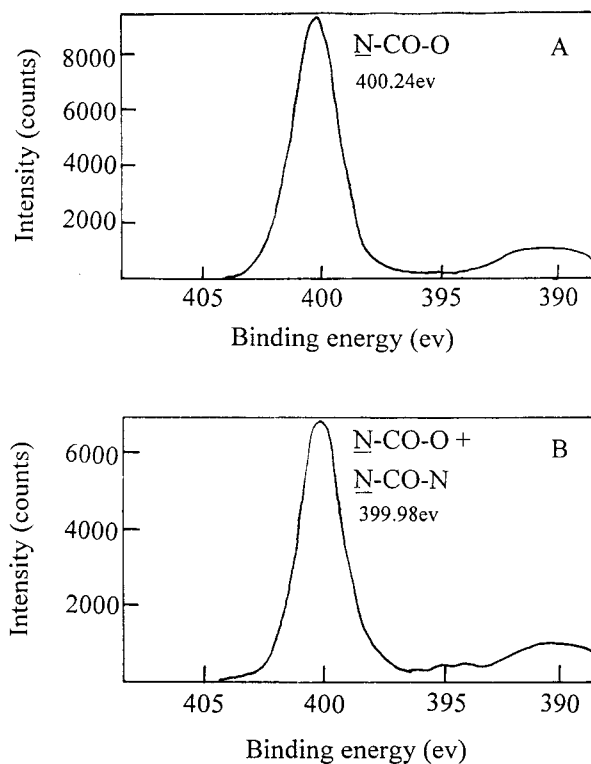


Figure 2 N_{1s} spectra of the films (A) PU and (B) PU-CH measured by using XPS.

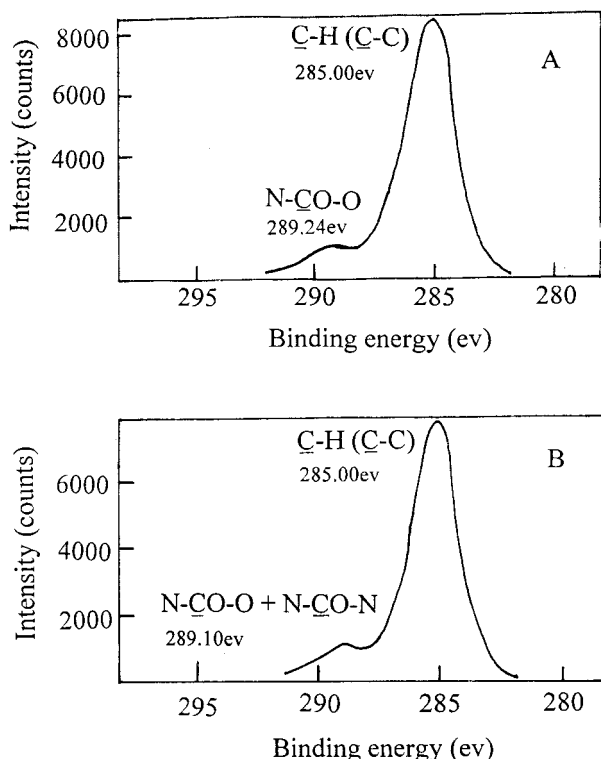
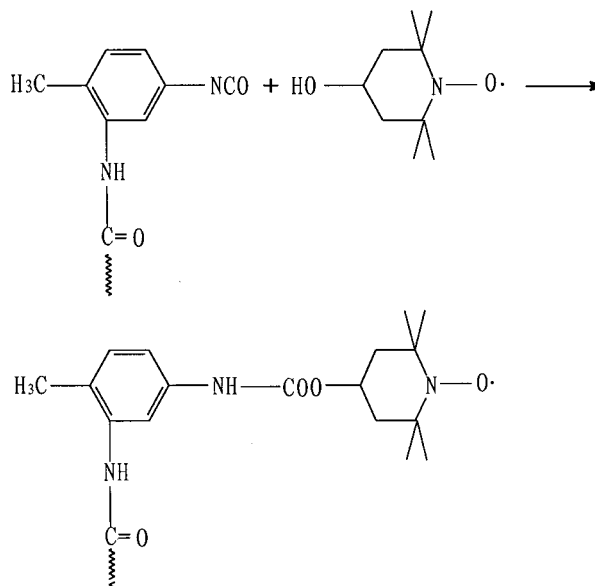


Figure 3 C_{1s} spectra of the films (A) PU and (B) PU-CH measured by using XPS.

on the surface of the film repelled hard segment units in PU, resulting in the decrease of N content on the surface. Theoretically, N and C contents of the chitosan unit should be lower than those of PU. Hence, according to this repelling assumption and strength ratio of N_{1s} , the ratio between the chitosan unit and the hard segment unit in PU on the surface of the PU-CH film was calculated to be 3 : 2. However, according to the composition used in sample preparation, this ratio should be 1 : 4 in the film. Therefore, chitosan was proved to be enriched on the surface of the film PU-CH.

Prior to the ESR measurements, the reaction of 4-hydroxy-TEMPO with PU-CH or PU prepolymers is shown as Scheme 1. Figure 4 shows the ESR for 4-hydroxy-TEMPO in (A) EA solution, covalently bonded to the prepolymers of (B) PU-CH and of (C) PU, respectively, at room temperature. It was observed that there is a distinct difference between the 4-hydroxy-TEMPO in EA solution and the 4-hydroxy-TEMPO in the films PU-CH and PU. In EA solution, the 4-hydroxy-TEMPO molecules can tumble freely, exhibiting three sharp lines with nearly uniform peak heights. In contrast, in both films, the rotational motion of the covalently bonded 4-hydroxy-TEMPO



Scheme 1 The reaction of 4-hydroxy-TEMPO coupled with polyurethane prepolymers.

is severely hindered by the rigid microenvironment. The ESR spectra of the films PU-CH and PU become broadened and unsymmetrical due to the slow motion of the 4-hydroxy-TEMPO, which

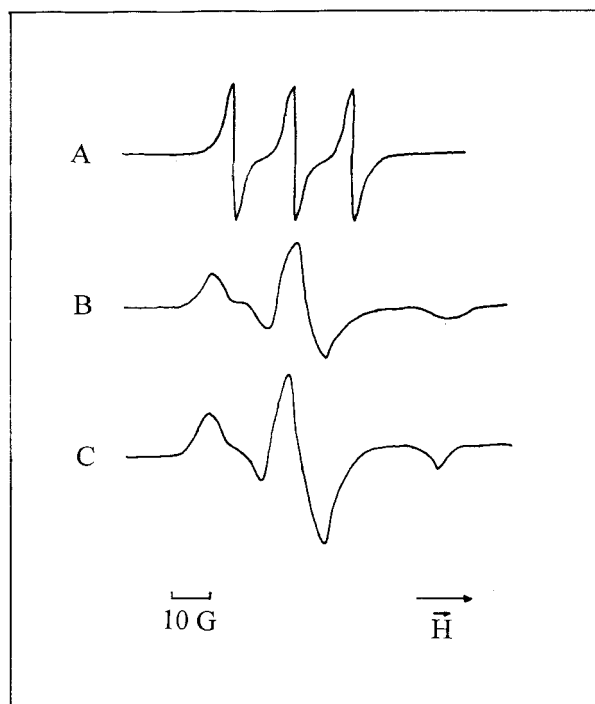


Figure 4 ESR spectra of 4-hydroxy-TEMPO in (A) EA solution, (B) coupled with PU-CH, and (C) coupled with PU at room temperature.

has anisotropical paramagnetic parameters (hfs and g-factor). The ESR spectra as shown in Figure 4(B) and (C) are usually called powder spectra. According to the line shape of ESR spectra, the rate of the rotational motion of 4-hydroxy-TEMPO molecules can be calculated and described with the rotational correlation time τ_c . Figures 5 and 6 show ESR spectra of 4-hydroxy-TEMPO coupled with PU-CH and with PU, respectively, measured at different temperatures. At a low temperature (approximately below 50°C), both the figures show typical powder patterns, indicating the very slow motion of the 4-hydroxy-TEMPO in the films. However, with increasing the temperature, the ESR spectra became more and more close to that for solution radicals [Fig. 4(A)], implying an increase in the freedom of molecular motions. It was observed that the spectra of the films broadened progressively with decreasing the temperature. The extrema outer line separation (ΔW) means the field difference between the left and right bands. At high temperatures (approximately above 100°C), ΔW decreased to approximately 35 G, which was characteristic of

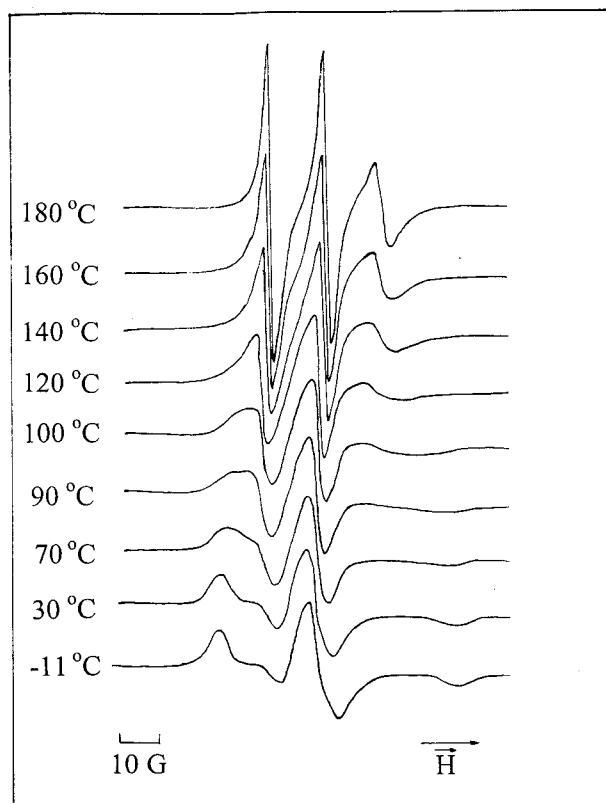


Figure 5 ESR spectra of 4-hydroxy-TEMPO coupled with PU-CH, measured at different temperatures.

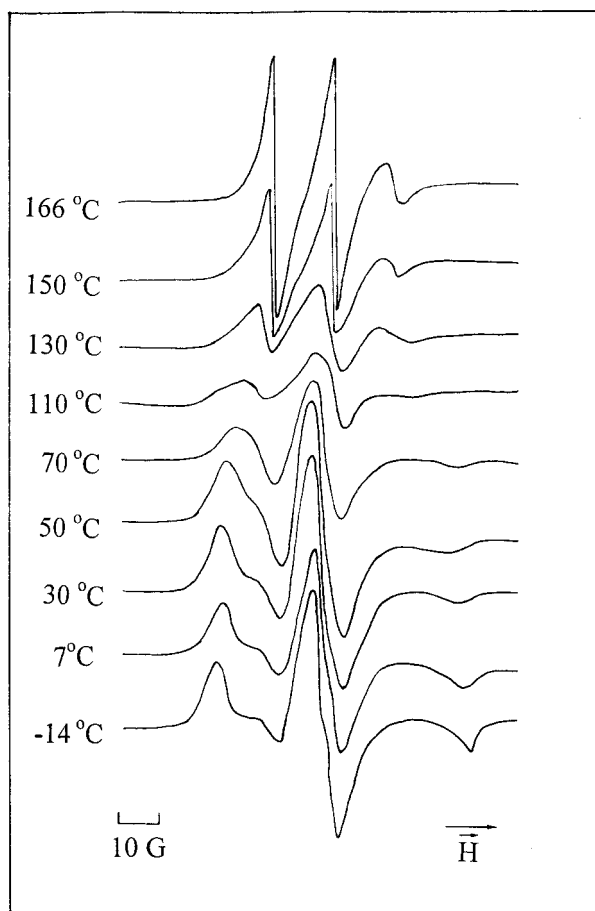


Figure 6 ESR spectra of 4-hydroxy-TEMPO coupled with PU, measured at different temperatures.

a relatively fast-tumbling spin probe. In view of the line shapes and their changes, the probe for the film PU-CH showed stronger features of powder spectra than that for the film PU. It indicates that a more restrained microenvironment exists in the film PU-CH than in the film PU, suggesting a reduced motion of the chain segments in the film PU-CH. The change in the ESR spectral line shape with temperature exhibits a nonmonotonic feature for the film PU in the temperature region from 110 to 130°C. This may relate to subtle changes in the mode of molecular motions, such as the anisotropy of the rotational motion, but the details remain to be a subject for the further study.

The ΔW is plotted against temperature in Figure 7. The T_{50G} for the films PU-CH and PU were 92 and 82°C, respectively. The measured values of T_{50G} are correlated with the first glass transition of polymers,¹³ and an empirical correlation between T_{50G} and T_g was established by

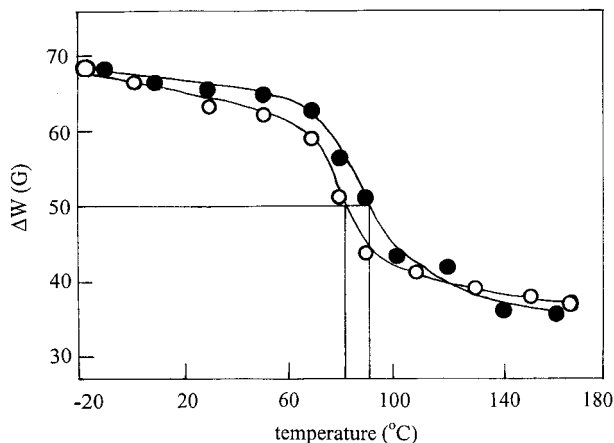


Figure 7 Plots of ΔW versus temperature for the (●) PU-CH and (○) PU.

$$T_{50G} = T_g / (1 - 0.03 T_g / \Delta H_a) \quad (3)$$

where ΔH_a is the tumbling activation energy of the probe. The T_{g1} of the films PU-CH and PU were evaluated to be 64 and 46°C, respectively.

The mobility of spin probes can be quantitated in terms of the rotational correlation time τ_c , which is calculated using the following equations²⁰:

$$\tau_c = 6.65 \times 10^{-10} \Delta H_{+pp} \times [(h_+/h_-)^{0.5} - 1] \quad (4)$$

$$\kappa = [H(\tau) - H(\tau \rightarrow 0)] / [H(\tau \rightarrow \infty) - H(\tau \rightarrow 0)] \times 100 \quad (5)$$

where τ_c is the rotational correlation time in seconds; h_+ is the height of the low field line; h_- is the height of the high field line; and ΔH_{+pp} is the peak-to-peak line width of the low field line (in Gauss). $H(\tau)$ is the line position (G) of the low field line; $H(\tau \rightarrow 0)$ and $H(\tau \rightarrow \infty)$ are these positions in the cases of low viscous solution and rigid powder states, respectively. Equation (5) is valid for the slow motion region ($\tau > 5 \times 10^{-9}$ sec).²² In this case, τ_c was found from the κ values according to the $\tau_c \sim \kappa$ plot given in Kuznetsov et al.²⁰ Thus, ΔH_a can be calculated by the following Arrhenius relation^{12,14}:

$$\Delta H_a = R [d \ln(1/\tau_c) / d(1/T)] \quad (6)$$

where R is gas constant. The Arrhenius plots of τ_c are shown in Figure 8. ΔH_a values for the probes in the films PU-CH and PU were evaluated from the slope of the lines to be 27.0 and 12.8 kJ mol⁻¹, respectively. It is well known that the

motion of the probe is affected by the free volume and mobility of the polymer chains. Hence, it could be concluded that the chains in the films PU-CH possessed smaller free volume and lower mobility at room temperature than those in the film PU, suggesting that the chitosan was grafted and crosslinked with PU to enlarge the molecular size and enhance the intermolecular bonding.

The TDA and TGA of the films PU-CH and PU are shown in Figure 9. It was observed that each film has two glass temperatures. For the film PU-CH, T_{g1} and T_{g2} were 63 and 163°C, respectively, and the decomposition temperature (T_d) was 276°C. However, for the film PU, the corresponding temperatures were 47, 163, and 242°C for T_{g1} , T_{g2} , and T_d , respectively. T_{g1} for the film PU-CH was 16°C higher than that for PU, and this is in good agreement with ESR results (64°C for the film PU-CH and 46°C for PU). In addition, the T_d for the film PU-CH was 34°C higher than that for the film PU. In view of thermal analysis results, it could be concluded that the film PU-CH had higher thermal stability than the film PU, owing to the covalent bonds between chitosan and PU prepolymers. It suggests that the chitosan exists as a macromolecules grafted and crosslinked with PU in the film PU-CH, rather than the original one having low molecular weight ($M_n = 6500$). If the chitosan did not react with PU, namely, it existed as a simple blend, the T_g and T_d of the film PU-CH would be lower than those of the film PU because the depolymerized chitosan would act as a plastifier. For a typical block copolymer, the ESR signal would contain two superimposed spec-

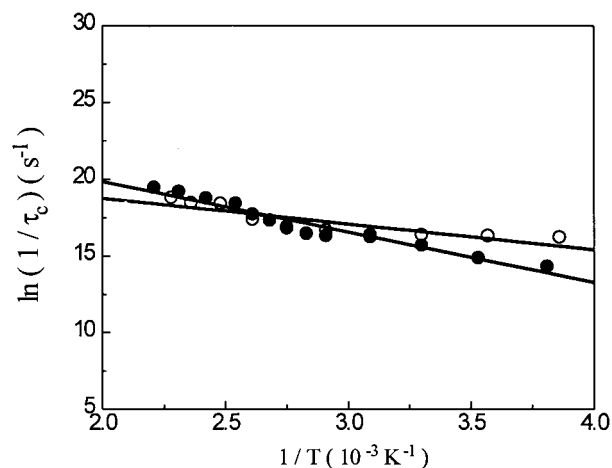


Figure 8 Arrhenius plots of rotational correlation time ($1/\tau_c$) for the spin probes in the (●) PU-CH and (○) PU films.

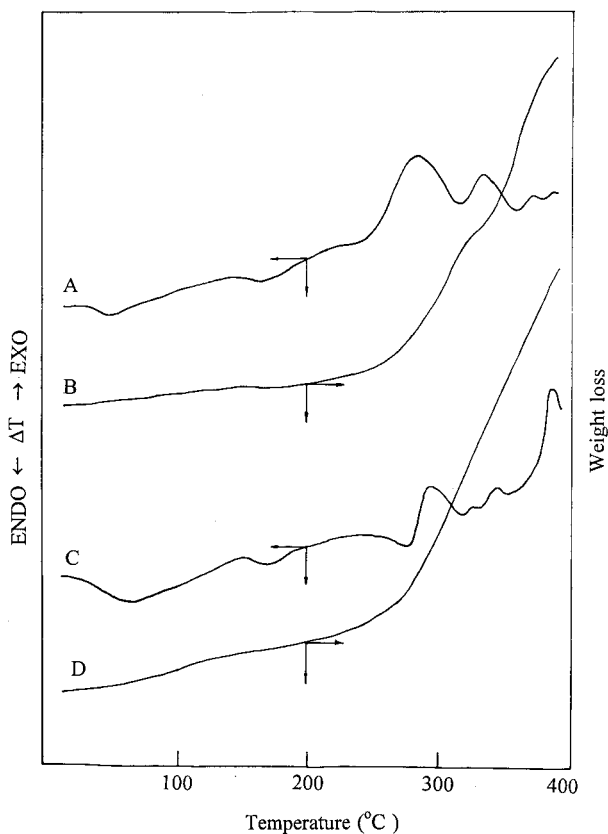


Figure 9 The DTA and TGA of the PU (A) and (B) and (C) and (D) PU-CH films.

tra with different T_{50G} , as reported by Kumler and Keinath.²¹ However, this phenomenon was not observed in this ESR work, implying that blocking was absent between the chitosan and PU. It was reported that the grafting and crosslinking would lead to a significant shift of the T_g of the PU to higher temperature,²² and the T_g of a grafted rubber was found to be 9°C higher than ungrafted rubber.²³ It is therefore further verified that chitosan in the film PU-CH was grafted and crosslinked with PU prepolymers, resulting in the reduction of the molecular motion.

The light transmittance of the films PU-CH and PU (T_r %) were measured to be 86.9 and 89.4%, respectively. Normally, the interface between two materials would cause losses in the optical transmission because of scattering and reflecting at the interface.²⁴ The similarity of T_r % between the films PU-CH and PU suggests that the strong bonding between the chitosan and PU exists in the film PU-CH. The grafting and crosslinking would lead to smaller domains, which increase the transparency of IPN materials.²⁵ With the evidence from UV, DTA, XPS, and ESR, we

conclude that the depolymerized chitosan in the film PU-CH plays an important role in forming a grafted IPNs.

CONCLUSIONS

A polyurethane-chitosan IPN (PU-CH) coating was prepared from a highly deacetylated and depolymerized chitosan, TDI, and castor oil. PU-CH coating was cured more speedily than PU in the absence of catalysts. The depolymerized chitosan was grafted and crosslinked with the PU prepolymer in the film PU-CH and highly enriched on the surface of the film. According to the empirical correlation between T_g and T_{50G} , the T_g values of the film PU-CH and PU were calculated from ESR data to be 64 and 46°C, respectively, which are in good agreement with the results measured by using TDA. The T_{50G} and ΔH_a of the spin probe for the film PU-CH were 10°C and 14.2 kJ mol⁻¹ higher than the corresponding values for the film PU, respectively, verifying that the chain mobility in the film PU-CH was obviously restrained. It was proven that the depolymerized chitosan was grafted and crosslinked with PU prepolymers and formed grafted IPNs in the film PU-CH, resulting in the enhancement of thermostability and optical transmittance and in a faster cure.

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