Properties and Interfacial Bonding of Regenerated Cellulose Films Coated with Polyurethane–Chitosan IPN Coating

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ABSTRACT: Water-resistant films were prepared by coating a castor oil-based polyurethane–chitosan (PU–CH), in which grafted interpenetrating polymer networks (IPNs) were produced, on a regenerated cellulose (RC) film. The tensile strengths of the coated films cured at 90°C for 5 min reached 853 kg cm^{-2} (dry state) and 503 kg cm^{-2} (wet state) and were obviously higher than those of the films of uncoated and coated with PU coating. Moreover, the coated films have excellent water resistivity, low vapor permeability, and good size stability, and their optical transmittance is even better than that of the RC film in the range of 400–800 nm. The interfacial structure of the coated films was investigated by using spectroscopy infrared, ultraviolet spectroscopy, transmission electron microscopy, and electron probe microanalysis. It was shown that the strong interfacial bonding with chemical and hydrogen bonds between the RC film and the coating exists. The PU prepolymer in the IPN coating penetrated through the interface into the RC film and partly crosslinked with the cellulose, forming a semi-IPNs. The chitosan in the PU–CH coating plays an important role not only in accelerating the cure of the coating but also in improving the mechanical properties and biodegradability of the coated film. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1313–1319, 1998

Key words: regenerated cellulose film; chitosan; IPNs; interfacial bonding; proerties; electron probe microanalysis

INTRODUCTION

The environmental pollution caused by extensive applications of nondegradable polymers has grown to a global problem.[1] The substitution for partial synthetic materials with cellulose and chitin can not only decrease the pollution but also save the petroleum resources. Some novel functional cellulose materials have been reported, such as a thermally stable cellulose benzenesulfonate,[2] high-strength and high-modulus cellulose fiber,[3] low-density polyethylene (LDPE)–cellulose composites,[4] the interpenetrating polymer networks (IPNs) from cellulose cinnamate,[5] and blend films of chitosan–fine cellulose powder.[6] The IPN materials derived from polyurethane and other polymers have good adhesive properties and can form a shared IPNs in the vicinity of the adhesive–substrate interface.[7] Moreover, it was also reported that a block polyurethane synthesized from 2,4-tolylene diisocyanate (TDI) and cellulose triactate (CTA) was proven to be biodegradable.[8]

It was well known that the hydrophilicity of regenerated cellulose films restrained their utilization in some fields. Thus, we have studied the water-resistant films prepared by coating polyurethane–poly(methacrylate-*co*-styrene) PU–(MA-St) semi-IPN coating[9] and polyurethane–nitrocellulose coating[10] on the regenerated cellulose (RC) films. The addition of the copolymer or nitrocellulose could not only accelerate curing the PU coating but also improve the mechanical proper-

ties of the coated films. In another article,[11] we have developed a castor oil-based polyurethane–chitosan (PU–CH) IPN coating, in which a depolymerized chitosan ($M_\eta = 6500$) substituted for the copolymer and catalyst. The results showed that PU–CH IPNs was formed by grafting and crosslinking the chitosan with the PU networks, and PU–CH coating cured much more readily than the corresponding PU. In the present work, we mainly investigated the mechanical properties, water resistivity, and biodegradability of the RC films coated with PU–CH. Simultaneously, with the help of infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, transmission electron microscopy (TEM), and electron probe microanalysis (EPMA), the interfacial bonding between the RC film and the coating in the coated film was analyzed and discussed.

EXPERIMENTAL

Preparation of the Coated Films

The RC film was prepared by coagulating cellulose cuoxam solution according to our previous work.[12] The viscosity-average molecular weight M_η of the cellulose (cotton linter purchased from the Chemical Fiber Manufacturer of Hubei, China) was measured to be 1.96×10^5 by using viscometry.

The synthesis of PU–CH coating and PU coating was described in another article.[11] PU–CH was dissolved in ethyl acetate to give 10% solid content, then coated on both sides of the RC films. The coated films were cured at 80, 90, 100, and 120°C for the desired time and coded as RCUH8, RCUH9, RCUH10, and RCUH12, respectively. Correspondingly, the RC film coated with PU was coded as RCU, which was cured at 90°C for 12 min. The films RCU and RCUH9-5, which were cured at 90°C for 5 min, were used for UV, TEM, SEM, and EPMA measurements. The films RCU and RCUH9-5 with thickness of 10 μm prepared by using the 5% solid content were used for IR analysis.

Measurements

The tensile strength (σ_b) and the breaking elongation (ε_b) of the films were measured with XLD-0.1 strength tester (The Second Tensile Testing Machine Manufacturer of Changchun, China) according to the National Standard of China,

GB4456-84. After immersed in the water for 1 h, the films were taken out and used as wet films for measurement. The water resistivity (R) of the films was evaluated from σ_b (dry) value in dry state and σ_b (wet) in wet state by the following equation:

$$R = \sigma_b(\text{wet})/\sigma_b(\text{dry}) \qquad (1)$$

The films with size of 10×10 cm^2 were immersed in the water for 24 h, then dried naturally. The average sizes of the films dried again, d, were recorded. The extent of constriction (S_c) of the films was estimated by

$$S_c = [(10 - d)/10] \times 100\% \qquad (2)$$

Moreover, the water vapor permeability (P) of the films was evaluated from evaporating amount of the water in a beaker (500 mL), which was sealed by the film, at 25°C and 75% relative humidity for 10 days, using

$$P = (w_0 - w_t)/10\,S \qquad (3)$$

where w_0 and w_t are the initial and final total weight (g) of the beaker, respectively. S is the effective covered area (cm^2) of the film used.

Biodegradation Test

Natural soil was used as biodegradation environment. The films were enclosed separately in nylon meshes and buried about 10 cm beneath the soil on our campus. The average values of the temperature and pH of the soil were measured to be 20°C and 6.8, respectively. After 7 days of burying, the films were taken out, then rinsed with water and dried in vacuum at the room temperature for 1 day. The biodegraded films were coated with gold, and then their surfaces were observed and photographed with Hitachi S-570 scanning electron microscopy (SEM). The tensile strength (σ_b) and weight loss W_{loss} (%) of the films biodegraded for 20 days were measured according to precious methods.[13]

Characterization

The optical transmittance of the films was measured with Shimadzu UV-160 spectrophotometer in the wavelength from 200 to 800 nm, and the thickness of the films used were the same (ap-
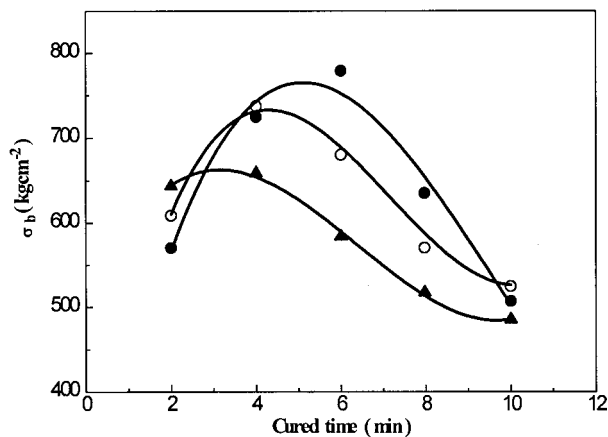
Figure 1   The effect of cured time on tensile strength (σ_b) of dry coated films. Cured temperatures: ($\bullet$) 80°C; ($\bigcirc$) 100°C; ($\blacktriangle$) 120°C.

Figure 2   The effect of cured time on tensile strength (σ_b) of wet coated films. Cured temperatures: ($\bullet$) 80°C; ($\bigcirc$) 100°C; ($\blacktriangle$) 120°C.

proximately 40 μm). IR spectra were recorded with a 170SX Fourier transform IR (FTIR) spectrometer. TEM of the section of the coated films was performed on a Hitachi 8100 electron microscope operated at 100 kV. Prior to the examination, the films were stained in the vapor of osmium tetraoxide for 72 h, then embedded in Epon 812. In order to obtain the information about the diffusion of the PU–CH coating to the RC film, one- and two-dimensional distribution of the N element on the section of the coated films were performed on an electron probe microanalyzer JXA-8800R (JEOL, Superprobe), which was equipped with a X-ray energy detector. The films were fixed directly between two steel bulks, which were coated with a conductive adhesive without nitrogen, and no other pretreatment was done for the films analysized.

RESULTS AND DISCUSSION

Effect of Cured Conditions on Properties

Figures 1 and 2 show that the tensile strengths of the films coated with PU–CH coating in dry and wet states changed with the cured time. The tensile strengths (σ_b) of the coated films increased to maximum with increasing the cured time, then decreased. It is worth noting that the σ_b of the dry films cured at every temperature used decreased when the cured time was more than 6 min. However, in the range of temperature adopted, the maximum σ_b of the dry and wet films increased with a decrease in the cured temperature and shifted to long cured time. It suggests that the
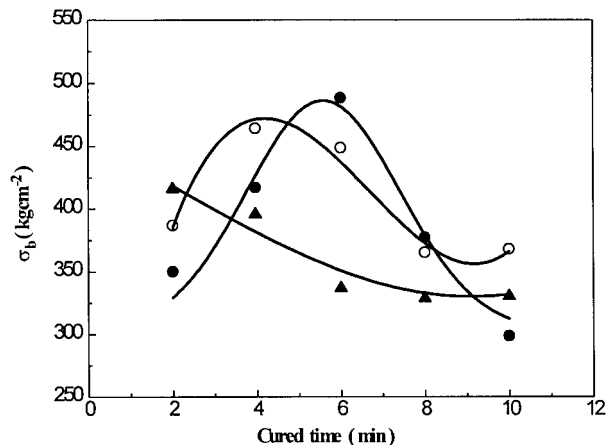
strength loss of the films was resulted from the excessive dehydration of the cellulose.

The cured time dependence of the vapor permeability (P) for the films RCUH9 is shown in Figure 3. P values of the films RCUH9 decreased rapidly with an extension of the cured time, then reached the minimum at the cured time of about 6 min, and finally increased with the further extension of the cured time, suggesting that the excessive extension of the cured time led to decreasing the water resistivity of the coated film. The cured time dependence of the extent of constriction (S_c) for the films RCUH9 is shown in Figure 4. The S_c, which represents the size stability, increased with increasing cured time until 6 min, then did not almost change. The results from P and S_c indicated that when the cured time was more than 6
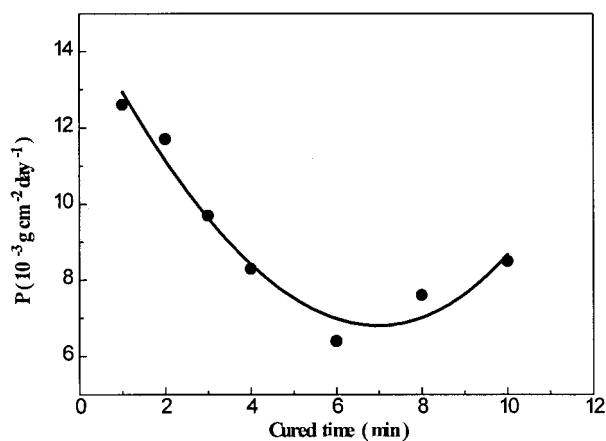

Figure 3   The effect of cured time on vapor permeability (P) of the coated film.
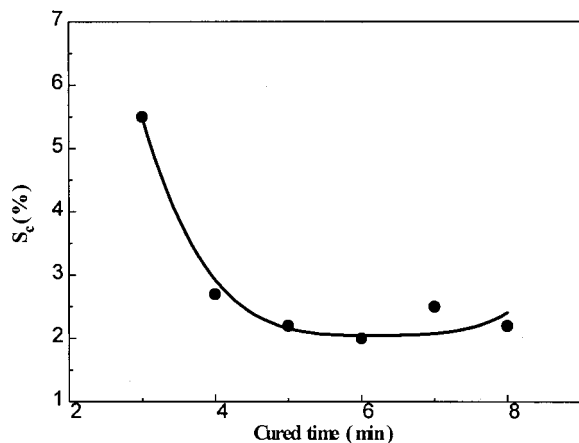
Figure 4 The effect of cured time on the extent of contraction (S_c) of the coated films.

min, the water resistivity of the coated film reduced. The tensile strength (σ_b), breaking elongation (ε_b), vapor permeability (P), and extent of constriction (S_c) of the films RCUH9-5, RCU, and RC are listed in Table I. It is clear that the mechanical properties and water resistivity of the film RCUH9-5 are much higher than those of the films RCU and RC.

Biodegradability of the Coated Film

The SEM of the films RCUH9-5 and RCU degraded by the microorganisms in soil are shown in Figure 5. A porous structure and fungal mycelia of both the films RCUH9 and RCU are observed, similar to the degradation of the regenerated cellulose films coated with PU–nitrocellulose.[10] It was indicated that both films RCUH9-5 and RCU could be biodegraded by the microorganisms in the soil, owing to the presence of the castor oil in both coatings. The tensile strength changes [$\Delta\sigma_b = \sigma_b$ (after biodegradation) $- \sigma_b$ (before biodegradation)] and weight loss (W_{loss}, %) of the films RC, RCU, and RCUH9-5 biodegraded in soil for 20 days were listed in Table II. Obviously, the extent of biodegradation for the films RCUH9-5 and RCU

was lower than that for RC film,[13] suggesting the PU component could inhabit the biodegradation rate. However, the film RCUH9-5 was more readily biodegrated than the film RCU due to the introduction of chitosan. The biodegradabilities and biodegradation dynamics of these films will be reported specially.

Interfacial Bonding

IR spectra of the films RCUH9-5 and RC and PU–CH coating are shown in Figure 6. For the film RCUH9-5, the band at 1534 cm^{-1} is assigned to the H-bonded N—H bending vibration between the N—H and C=O groups, and the band at 1653 cm^{-1} to H-bonded carbonyl.[14] It is worth noting that a strong absorbance in the spectrum of the RC film at 1642 cm^{-1} attributed to glucose carbonyl of the cellulose almost disappeared in the spectrum of the film RCUH9-5, suggesting that the glucose carbonyl group as a hemiacetal reacted with —NCO groups in the PU–CH coating. The band at 1725 cm^{-1} is attributed to the urethane carbonyl in PU–CH coating, as shown in Figure 6. The asymmetric peek with a shoulder for the film RCUH9-5 suggests that there is a superposition of 1725 cm^{-1} band and a new band assigned to cellulose ester groups (1700 cm^{-1}),[15] which was resulted from cellulose esterification with the —NCO groups of the coating. The band at 2273 cm^{-1} attributed to the residue of —NCO groups in the spectrum of the film RCUH9-5 significantly reduced, owing to the reaction with cellulose. Usually, the bands of nonbonded —OH and —NH$_2$ groups appear at 3450–3650 cm^{-1}. Compared with the spectrum for the RC film, the band at 3100–3500 cm^{-1} for the film RCUH9-5 was obviously broadened and shifted to lower wave number, suggesting the introduction of the much hydrogen bonds. In view of the IR analysis, the chemical and hydrogen bonds exist between PU–CH coating and cellulose.

Figure 7 shows the optical transmittance of the

Table I   The Comprehensive Propreties of the Films

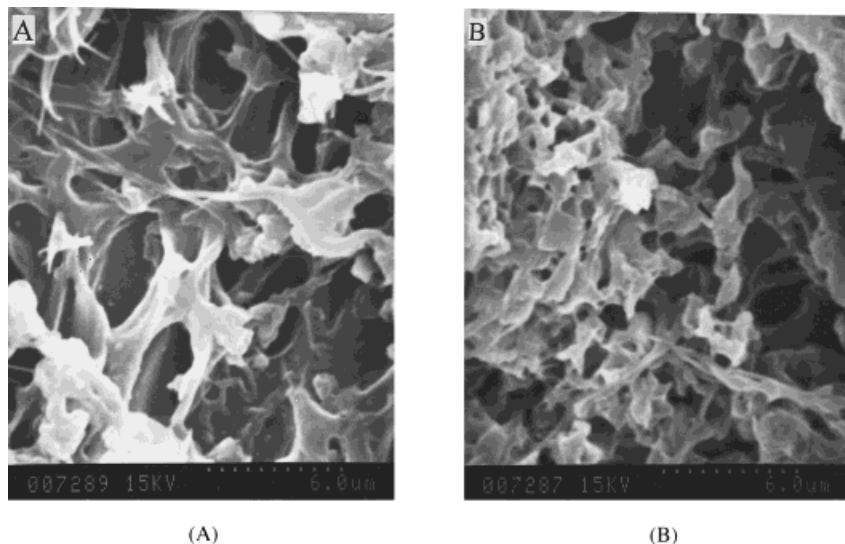| Films	σ_b (kg cm^{-2})		ε_b (%)		R	$P \times 10^3$ (g cm^{-2} day^{-1})	S_c (%)
	Dry	Wet	Dry	Wet			
RC	740	198	10	70	0.27	15.0	11
RCU	757	402	25	45	0.53	6.5	3
RCUH9-5	853	503	20	35	0.59	6.7	2

Figure 5 SEM of the films (A) RCUH9-5 and (B) RCU degraded by microorganisms.

films from 200 to 800 nm. The transmittances of both films RCUH9-5 and RCU were higher than that of RC film. Usually, the interface between two dissimilar materials will cause losses in optical transmission, where the light is scattered and reflected at the interface of dissimilar solid materials.[16] It is worth noting that the transmittance of the PU coating was higher than that of PU–CH coating,[11] but the film RCUH9-5 has higher transmittance than the film RCU. The results prove that a strong interfacial bonding between the RC film and the coating exists in the film RCUH9-5. It could be regarded that the excellent transmittance reflected a high crosslinking in the interface of the coated films caused by the presence of the chitosan. The crosslink density and the level of internetwork grafting in IPNs could enhance their transparence.[17]

Figure 8 shows TEM photographs of the section of the films RCUH9-5 and RCU. The middle regions of the photoes are coating layers with approximately 2 μm deep, and the bottom is cellulose. The interface between the epon and the coating is distinct, and some impurities of the osmium precipita-

tion appear in the vicinity of the interface. It was observed that the interface between the coating and cellulose of the films RCUH9-5 and RCU appears
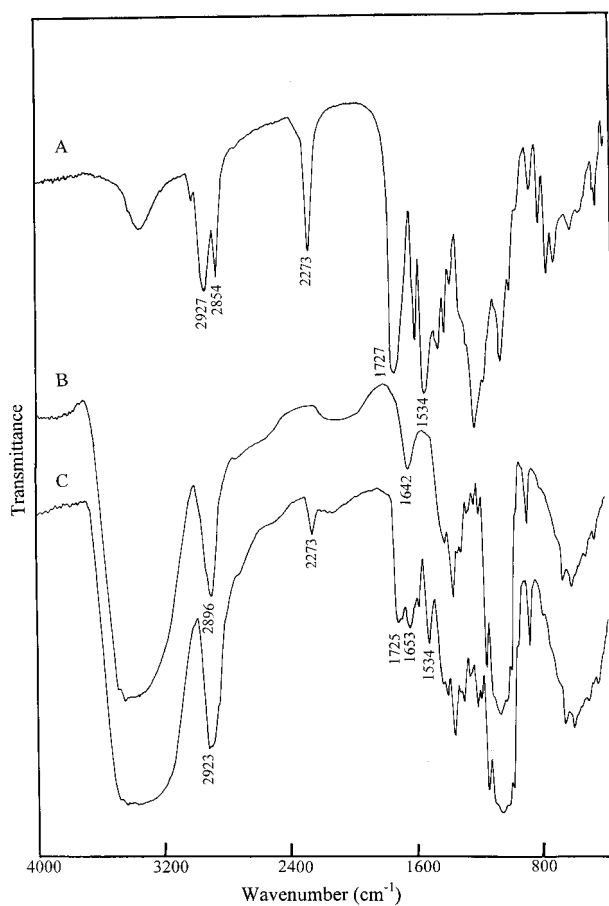

Figure 6 IR spectra of the films (A) PU–CH, (B) RC, and (C) RCUH9-5.

Table II The Tensile Strength Changes ($\Delta\sigma_b$) and Weight Loss (W_{loss}, %) of the Films Biodegraded in Soil for 20 Days

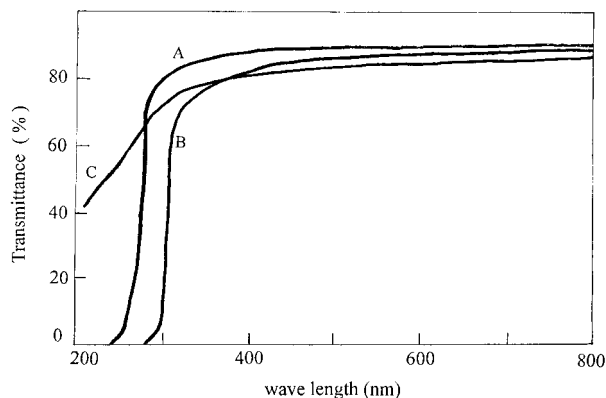| Films	$\Delta\sigma_b$ (kg cm^{-2})	W_{loss} (%)
RC	−356	32.5
RCU	−162	9.5
RCUH9-5	−204	14.3

Figure 7   The optical transmittance of the films (A) RCUH9-5, (B) RCU, and (C) RC.

as a tight adhesion. The results supported the conclusion from the transmittance of the films.

Figure 9 shows the one- and two-dimensional distributions of the N element on the sections of the films RCUH9-5 (A) and (B) and RCU (C) and (D) measured by EPMA. It was observed that the total thickness of the coated film RCUH9 or RCU is approximately 40 μm and that of the coating layer measured by TEM is 2 μm. The one-dimensional distribution of N element on the cross-section of RCUH9-5 [Figure 9(A)] shows that N content on both sides was higher than that in the middle, indicating that PU–CH coating penetrated into the RC films. In view of Figure 9(A), the thickness of the coating layer together with its penetrating layer of the film RCUH9-5 was calculated to be 6 μm. Hence, the diffusion of PU–CH coating to the RC film is approximately 4 μm deep on each side. N content in the center of the section gave rise to a bit, suggesting the symmetrical penetration and superposition of the PU–CH coating from side to center. However, the one-dimensional N element distribution on the section of the film RCU [Figure 9(C)]

exhibited a broad N region, suggesting that the penetration of PU coating to the RC film was speedier than that of PU–CH coating. It was regarded that the grafted chitosan in the PU–CH coating prevented the diffusion of the PU prepolymer to RC films. Based on these results, it could be concluded that while forming the grafted IPNs in the PU–CH coating,[11] the PU prepolymer molecules simultaneously penetrated into the RC film, in which PU reacted with cellulose, producing another semi-IPNs. It was regarded that a shared network[13] of PU crosslinked with cellulose and chitosan exists in the N diffusion region of the RCUH9-5 film, resulting in a strong interfacial bonding in the coated film.

CONCLUSION

The water-resistant films were satisfactorically prepared by curing the PU–CH IPN coating on the surface of the RC films at 70–90°C for 5 min. The films coated with PU–CH not only could be cured more readily but also had the more excellent water resistivity, mechanical strength, optical transmittance, and biodegradability than the film with the PU coating. In the film RCUH9-5, a gradient transition layer resulted from the penetration of the PU in PU–CH coating is approximately 4 μm deep, in which the PU prepolymer penetrated into the RC film and formed other semi-IPNs crosslinked with the cellulose. The PU content penetrated into the cellulose of the film RCU is more than that of the film RCUH9-5, in which grafted chitosan in the PU–CH IPN coating prevented the diffusion of the PU molecules. This is beneficial not only in saving the coating but also in accelerating the cure of coated film. The depolymerized chitosan in the PU–CH coating plays an important role in forming a strong
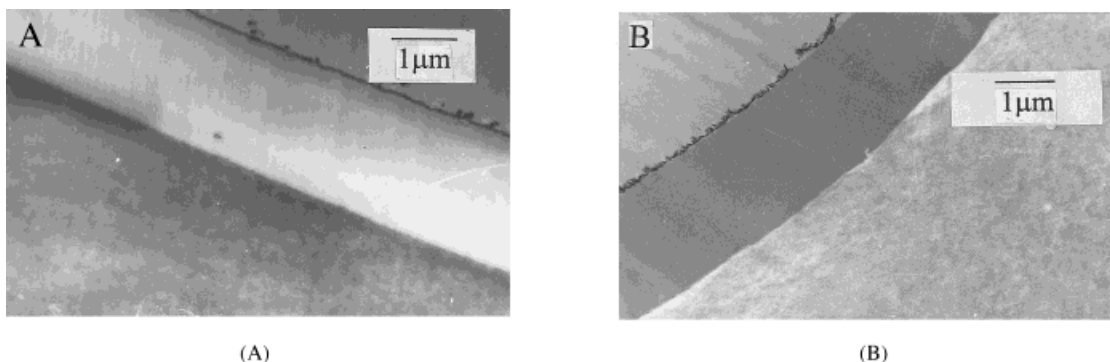

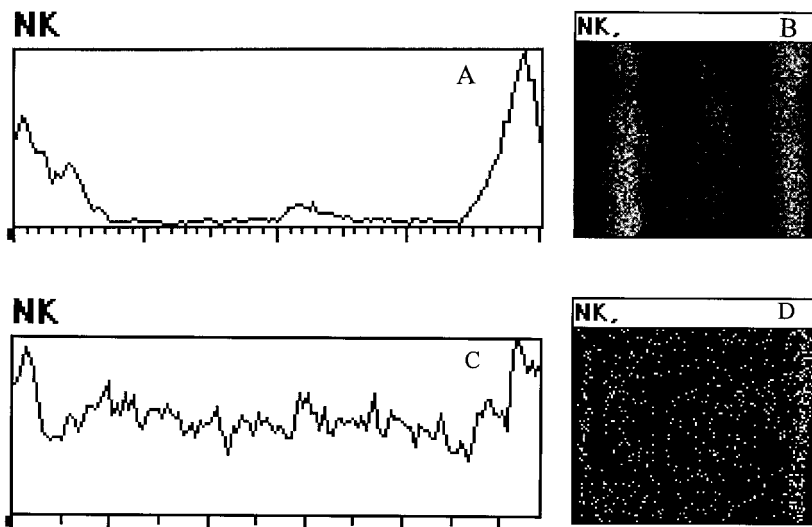**Figure 8**   TEM of sections of (A) RCUH9-5 and (B) RCU films.

Figure 9 Nitrogen distribution on sections of the films. RCUH9-5: (A) one-dimensional; (B) two-dimensional. RCU: (C) one-dimensional; (D) two-dimensional. Both films were measured by using EPMA.

interfacial bonding between the RC film and the coating layer by crosslinking and grafting with PU, resulting in enhancement of the properties mentioned above for the coated film.

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