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# STUDY ON THE PROPERTIES AND INTERFACIAL STRUCTURE BETWEEN REGENERATED CELLULOSE FILM AND POLYURETHANE/POLY(METHYL ACRYLATE) IPN COATING

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# STUDY ON THE PROPERTIES AND INTERFACIAL STRUCTURE BETWEEN REGENERATED CELLULOSE FILM AND POLYURETHANE/POLY(METHYL ACRYLATE) IPN COATING

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## ABSTRACT

Interpenetrating polymer networks (IPN) coating were synthesized from castor oil-based polyurethane (PU), methyl acrylate (MA), and coated onto the surface of regenerated cellulose (RC) film to obtain biodegradable water-resistant films. The tensile strength ($\sigma_b$), water resistance (*R*), water vapor permeability (*P*) percent light transmittance (*T*) and biodegradation rate of the coated films cured at 80°C for 5 minutes changed with the content of methyl acrylate in the coating. The introduction of methyl acrylate can enhance the water resistance, but reduce the biodegradation rate of the films. The most excellent values such as $\sigma_b$, 444 kg cm$^{-2}$ in wet state, *R*, 0.59, *P*, $3.2 \times 10^{-2}$ mg cm$^{-2}$ day$^{-1}$ were obtained at 30 wt% methyl acrylate in the coating. The interfacial bonding of the coated film was investigated with infrared spectroscopy (IR), ultraviolet spectroscopy (UV), transmission electron microscopy (TEM), electron probe micro-

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analysis (EPMA), and differential thermal analysis (DTA). The results showed that the coated films exist strong interfacial bonding caused by covalent and hydrogen bonds between the RC film and the coating. Furthermore, while there was formation of IPN in the coating, the PU prepolymer in the coating penetrated into the RC film and crosslinked with the cellulose formed another semi-IPN.

## INTRODUCTION

The environmental pollution caused by extensive application of plastics made from petroleum has become a serious problem [1]. Therefore, the use of polymers from renewable resources has attracted much attention because of their biodegradability and potential as substitutes for some petrochemicals derivatives. Some of these polymer plastic films that can be biodegraded by microorganisms in soil and seawater have been developed [2-4]. It was well known that plant cellulose is the most abundant biopolymer on earth which can be readily available and decomposed by microorganisms, the residues of the degraded product are not harmful to environment, it is an environmental friendly material [5]. Thus, the application of cellulose as films and containers is recently promising. However, plastics made from cellulose alone are water-sensitive due to the hydroxy groups in the main chain, and therefore limits the wide application of the cellulose. Various water-proof films and products such as cellulose triacetate films [6], and cellulose films coated with coatings such as nitrocellulose [7], polyurethane/chitosan [8], and polyurethane/nitrocellulose [9], etc. have been developed.

It was reported that the good mechanical properties and water resistance of the materials mainly depends on the good adhesion between the coating layer and the film. The interpenetrating polymer networks (IPN) materials derived from polyurethane and other polymer have good adhesive properties and can form a shared IPN in the vicinity of the adhesive/substrate interface [10]. For this reason, our laboratory has developed a research program for exploring the possibility of synthesizing a large number of biodegradable polyurethane interpenetrating networks coating from natural resources. In the present work, we mainly discussed the interfacial structure and properties of the regenerated cellulose (RC) films coated with castor oil-based polyurethane/poly(methyl acrylate) (PU/PMA) IPN coating by using transmission electron microscopy (TEM), electron probe microanalysis (EPMA), infrared spectroscopy (IR), ultraviolet spectroscopy (UV), differential thermal analysis (DTA), and scanning electron microscopy (SEM). The biodegradability and strength measurement of dry and wet films are also investigated.

## EXPERIMENTAL

### Raw Materials and Treatment

Castor oil (chemically pure) was dried by azeotropic distillation with toluene. Toluene diisocyanate (TDI, ration of 2,4-TDI/2,6-TDI is 80/20 by weight) was redistilled under reduced pressure at 120°C before use. Methyl acrylate (MA, chemically pure) was freed from inhibitor by reduced pressure distillation. Benzoyl peroxide (BPO) was recrystallized from chloroform. Stannous octoate (SnOc, chemically pure) was purchased from Aldrich Chemicals. All other reagents were analytically pure.

### Preparation of PU/PMA IPN Coating

Castor oil (50 g) was reacted with toluene-2,4-diisocyanate (TDI, 16.4 g) to maintain the NCO/OH ratio at 1.3. The reaction was carried out at 45°C with continuous stirring for 2 hours. The polyurethane (PU) prepolymer was isolated as a thick syrup. Then the PU/PMA IPN coating were synthesized by charging the PU prepolymer into a three-necked flask. To this, the mixture of methyl acrylate and 0.5% benzoyl peroxide was added under nitrogen atmosphere, The mixture was stirred at room temperature for 10 minutes to form a homogenous solution. Then the temperature was raised to 60°C to initiate the double bond of methyl acrylate and castor oil copolymerization. After stirring for 1 hour, the ethyl acetate as diluting agent (solid content 12%) and stannous octoate as catalyst were added.

### Film Preparation

The regenerated cellulose (RC) film was prepared according to L. Zhang *et al*. [11]. The viscosity-average molecular weight $M_\eta$ of the cotton linter cellulose was measured to be $1.54 \times 10^5$ by using Ubbelohde viscometry. The PU/PMA coating was coated on both surfaces of the RC films. the coated films were stayed at room temperature for 24 hours, then cured at 80°C for 5 minutes. A series of the films coded as C-UM$_0$, C-UM$_1$, C-UM$_2$, C-UM$_3$, C-UM$_4$, C-UM$_5$, and C-UM$_6$ corresponding to MA content (wt%) in PU/PMA coating of 0, 10, 20, 30, 40, 50, and 60 wt%, respectively.

## Measurements of Properties

The tensile strength ($\sigma_b$) and breaking elongation ($\varepsilon_b$) of the coated films in dry and wet state, which was soaked in water for 1 hour at room temperature before testing, were measured with an Electronic Strength Tester AG-A (Shimadzu Co.) according to the Chinese standard method (GB, 4456-84). The water resistance ($R$) of the films was evaluated from $\sigma_b$ (dry) value in the dry state and $\sigma_b$ (wet) in the wet state by the following equation:

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

The water vapor permeability ($P$) of the films was measured from evaporating amount of the distilled water in a 25 x 40 mm weighing bottle, which was sealed by the film at room temperature, 1 atm, and 75% relative humidity for 15 days, and calculated as follows:

$$P = (\mathrm{W_f}\ \ (\mathrm{W_o})/15\mathrm{S} \tag{2}$$

Here $\mathrm{W_f}$ and $\mathrm{W_o}$ are the final and initial total weight (mg) of the weighing bottle, S is the effective area of the used films ($\mathrm{cm}^2$).

Moreover, the percent light transmittance ($T$) of the films was measured in the wavelengths of 200-800 nm by using a Shimadzu UV-160 spectro-photometer, and the thickness of the films used were about 35 μm.

## Characterization of Films

IR spectra of the films were recorded with Nicolet 170SX FT-IR spectrometer. DTA was performed on a Thermal Analyzer DT-40 (Shimadzu Co.). Platinum pans were used for the analysis, and the films were cut to 1 mm length and 1 mm width, then analyzed under a nitrogen atmosphere from 30 to 600°C at a heating rate of 20°C/minute. TEM of the section of the coated film was performed on a JEM 100-XT Electron Microscope operated at 100kV. Prior to examination, the film was stained in the vapor of Osmium tetraoxide for 72 hours, and then embedded in Epon resin 812. Ultrathin sections were obtained by sectioning on LKB-8800 ultratome. In order to obtain the information about the diffusion of the PU/PMA coating to the RC film, a one- and two- dimensional nitrogen element on the section of the coated film was determined on an Electron Probe Microanalyzer JXA-8800R (JEOL Superprobe), which was equipped with a X-ray energy detector and operated at 10kV. The film which was coated with a conductive adhesive without nitrogen element was fixed directly between two steel sheets.

### Methods of Biodegradation

Natural soil was used as the biodegradation environment. The films (5 x 5 $\mathrm{cm}^2$) were enclosed separately in nylon meshes (2 x 2 $\mathrm{mm}^2$ mesh size), and buried about 10 cm beneath the soil on our campus. The average values of the temperature, relative moisture, and pH of the soil were measured to be 24°C, 30% and 5.8, respectively. After 30 days of degradation, the films were taken out, then rinsed with water and dried in vacuum at 50°C for one day. The weight loss ($\mathrm{Wt}_{\mathrm{loss}}$ %) of the films were calculated according to the following equation:

$$Wt_{\mathrm{loss}}\% = (W_{\mathrm{b}}(W_{\mathrm{a}})/W_{\mathrm{b}} \times 100\% \tag{3}$$

Here $W_{\mathrm{b}}$ and $W_{\mathrm{a}}$ are the total weight (mg) of the films before and after biodegradation. Then the films were coated with gold, and their surface were observed and photographed with Hitachi S-570 Scanning Electron Microscopy.

## RESULTS AND DISCUSSION

### Effect of Methyl Acrylate Content on the Properties of the Films

Figure 1 shows the relationship between water vapor permeability ($P$) of the coated films and the methyl acrylate content of the coating. The $P$ decreased with increasing methyl acrylate content until 30 wt% of methyl acrylate, and then increased, but all the $P$ of coated film are lower than the uncoated RC film (in Table 1). It was observed that the films of C-$\mathrm{UM}_2$ and C-$\mathrm{UM}_3$ coated with coating in which the content of methyl acrylate is 20-30 wt% have excellent water resistance. The great permeability such as film C-$\mathrm{UM}_6$ is possibly due to the microphase-separated structure in the coating layer [12]. Furthermore, the water-resistance ($R$) of the coated films C-$\mathrm{UM}_3$ and C-$\mathrm{UM}_6$ (Table 1) are far higher than the uncoated RC film. These results indicated that the RC films coated with coating have more better water resistance than uncoated RC film and a certain content of the methyl acrylate in the coating can significantly improve the water resistance and mechanical strength of the coated films.

The optical transmittance of the films C-$\mathrm{UM}_3$, C-$\mathrm{UM}_6$ and RC from 200-800 nm are shown in Figure 2 and Table 1. Usually, the interface between two

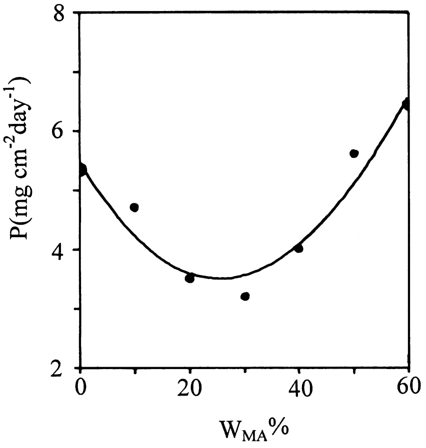

**Figure 1.** The influence of methyl acrylate content on the water vapor permeability (*P*) of the coated films at 25°C.

dissimilar materials will cause a loss in optical transmission because the light is scattered and reflected at the interface of dissimilar solid materials [13]. In Figure 2 and Table 1, the maximum percent light transmittance of film C-UM$_3$ was even higher than that of RC film at visible wavelengths (500-800 nm). The results suggested a strong interfacial bonding between the RC film and the coating.

## Interfacial Bonding Mechanism

The FT-IR spectra of the coating PU/PMA, RC and the C-UM$_3$ film are shown in Figure 3. For the RC film, the band at 1642 cm$^{-1}$ assigned to glucose

TABLE 1. Mechanical Properties ($\sigma_b$, $\varepsilon_b$), Water Resistance (*R*), Water Vapor Permeability (*P*), Percent Light Transmittance (*T*) and Weight Loss (*Wt*$_{loss}$) of Biodegradation for the Films

| | ($\sigma_b$/kg cm$^{-2}$ | | ($\varepsilon_b$/% | | | $P \times 10^2$ | *T*/% | *Wt*$_{loss}$ |
|---|---|---|---|---|---|---|---|---|
| Film No. | Dry | Wet | Dry | Wet | R | mg cm$^{-2}$ day$^{-1}$ | 800 nm | % |
| RC | 721 | 178 | 12 | 70 | 0.25 | 52.6 | 89.3 | 92.3 |
| C-UM$_0$ | 742 | 393 | 27 | 43 | 0.53 | 5.3 | 89.3 | 15.7 |
| C-UM$_3$ | 753 | 444 | 24 | 37 | 0.59 | 3.2 | 90.3 | 11.2 |
| C-UM$_6$ | 759 | 417 | 22 | 33 | 0.55 | 6.4 | 88.6 | 8.9 |

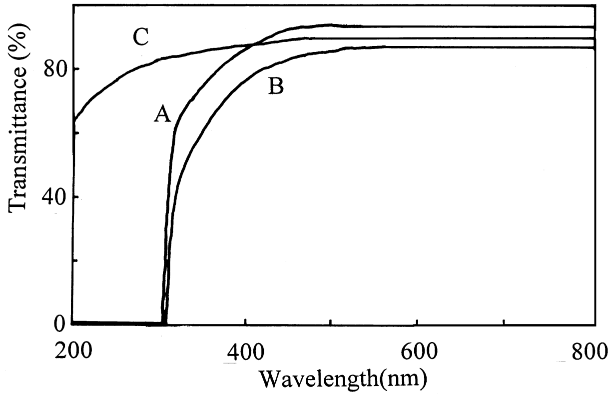

**Figure 2.** The optical transmittance of the films (A) C-$UM_3$, (B) C-$UM_6$, and (C) RC.

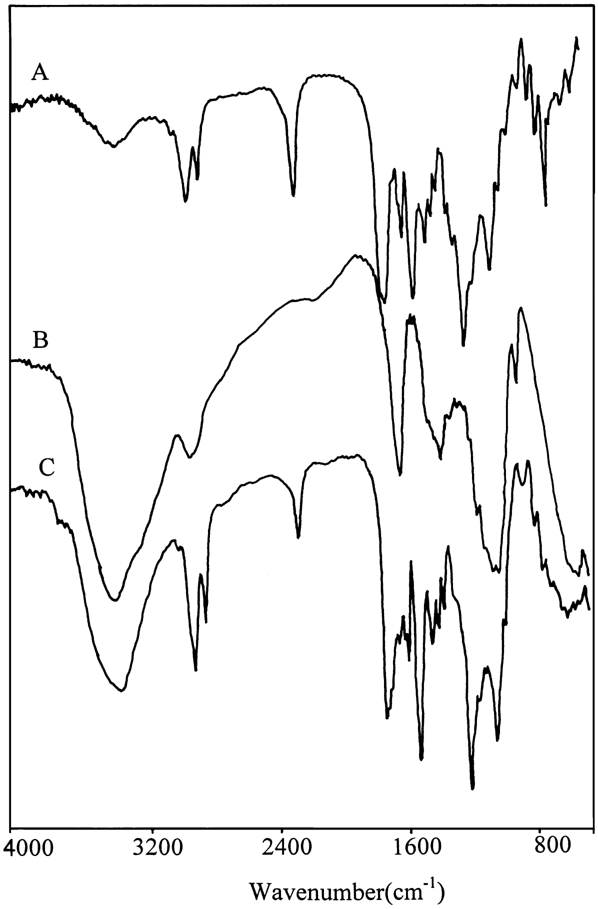

**Figure 3.** IR spectra of the films PU/PMA (A), RC (B), and C-$UM_3$ (C).

carbonyl of the cellulose almost disappeared in the spectrum of the film C-UM$_3$, suggesting that the glucose carbonyl group as a hemiacetal reacted with -NCO group in PU/PMA coating. The band at 1733 cm$^{-1}$ is attributed to the urethane carbonyl in PU/PMA coating. The asymmetric peak with a shoulder for the film C-UM$_3$ indicates that there is a superposition of the 1733 cm$^{-1}$ band and a new band assigned to cellulose ester groups (1700 cm$^{-1}$) [14], which was formed from cellulose esterification with the -NCO groups of the coating. The intensity of the band at 2273 cm$^{-1}$ attributed to the residue of -NCO groups in the film C-UM$_3$ was markedly reduced compared with the absorption intensity of the coating, also indicating the PU prepolymer molecules of PU/PMA coating to penetrate into the cellulose and esterfication to take place. Usually, the bands of nobonded -OH groups appear at about 3400 cm$^{-1}$, compared with the IR spectrum for the RC film, the absorption band of -OH at 3385 cm$^{-1}$ for the film C-UM$_3$ was broadened and shifted obviously to lower wavenumber, suggesting the formation of much hydrogen bonds between cellulose and the coating. The appearance of a new band at 1653 cm$^{-1}$ for the film C-UM$_3$ assigned to H-bonded carbonyl also verified the introduction of much hydrogen bonds between cellulose and the coating [15]. In view of the IR analysis, the hydrogen and chemical bonds exist between PU/PMA coating and cellulose.

Figure 4 shows the DTA curves of the films of RC, C-UM$_3$, and PU/PMA coating. In the curve of RC film, an endothermic process at 350°C was observed, showing that cellulose degraded completely by the loss of -OH groups and the breakdown of the pyranosic rings [16]. In the DTA curve of C-UM$_3$ film, the

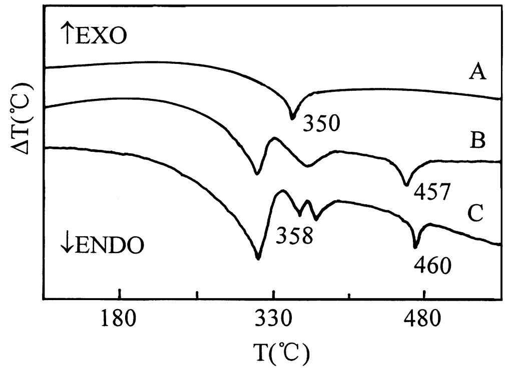

**Figure 4.** DTA curves of the films of RC (A), PU/PMA coating (B), and C-UM$_3$ (C).

endothermic peak corresponding to the temperature of decomposition of cellulose was shifted toward a higher temperature (358°C), implying greater thermal stability. As shown in Fig. 4, there were three endothermic peaks appeared at 312°C, 366°C, and 457°C, respectively, in the DTA curve of the PU/PMA coating. But, the endothermic peaks in the DTA curve of C-UM$_3$ film shifted to higher temperature, and appeared at 316°C, 370°C, and 460°C correspondingly. The enhancement in thermal stability of the coated film confirmed the strong interactions between PU/PMA coating and cellulose film.

Figure 5 shows the TEM photographs of the section of film C-UM$_3$. The dark region stained by Osmium tetraoxide in the middle of the photo is PU/PMA coating layer with about 2 mm deep, and the bottom is cellulose bulk. It was observed that the interface between the coating layer and epon (top in Figure 5) was distinct, and some impurities of the Osmium precipitation appeared in the vicinity of the interface. However, the interface between the coating and cellulose bulk was indistinct, indicating a tight adhesion between the interface of the coating and RC film.

The photographs of one-dimensional (A) and two-dimensional distribution of nitrogen element (B) on the cross-section for the film C-UM$_3$ analyzed by the electron probe X-ray energy spectrograph are shown in Figure 6. It was observed that the nitrogen of the film was detected not only in the coating layer but also in the RC film, furthermore, the nitrogen content on both sides was high-

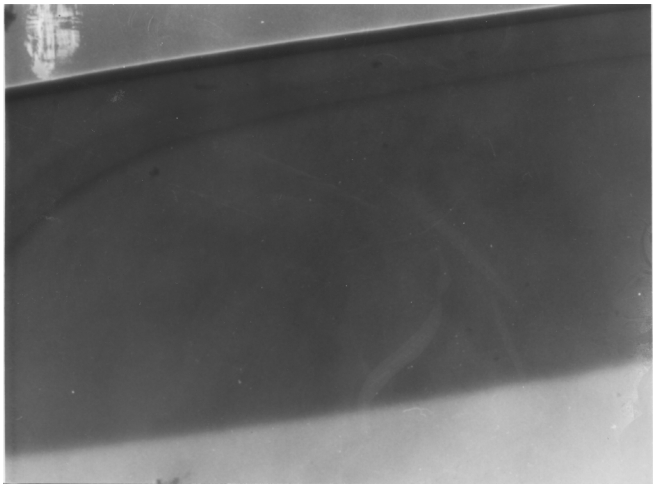

**Figure 5.** TEM of the film C-UM$_3$.

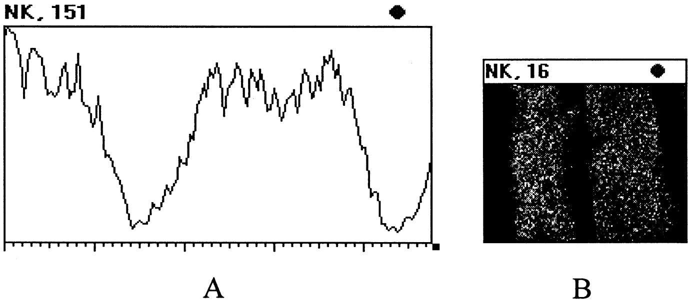

**Figure 6.** Nitrogen distribution on the section of the film C-$UM_3$ (A, one-dimensional, B, two-dimensional) measured by EPMA.

er than that in the middle region, and decreased gradually from two sides to the middle of the coated film, indicating that the PU prepolymer in the coating penetrated into the RC film. In view of Figure8 6A, the thickness of the coating layer together with its penetrating layer of the film C-$UM_3$ was calculated about 6 μm, the coating layer was about 2 μm deep according to TEM result, hence, the PU penetrating region for each side in the RC film was about 4 μm.

Based on these results, the interfacial bonding mechanism can be described that while forming IPN in the coating layer, the PU prepolymer of the coating penetrated into the RC film, in which the -NCO groups of the PU reacted with cellulose, thus, in the penetrating layer producing another semi-IPN. It was regarded as a shared network of PU crosslinked with cellulose existed in the penetrating layer and copolymer of castor oil and methyl acrylate [8-10]. Therefore, the strong interfacial bonding was sustained by the covalent bonds and the hydrogen bonds between the coating and RC film.

## Biodegradability of the Coated Film

The SEM photographs of the film C-UM3 biodegraded by the microorganisms in soil and the original are shown in Figure 7. Before biodegradation, the surface of the coated film was smooth and dense (Figure 7A), but after degradation in soil for 30 days, a pour and fungal mycelia on the surface of the film was observed (Figure 7B). It suggested that the RC films coated with PU/PMA coating could be biodegraded by the microorganism in soil. The percent weight loss ($Wt_{loss}$%) of the film RC, C-$UM_0$, C-$UM_3$, and C-$UM_6$ degraded in soil for 30 days were listed in Table 1. Obviously, the rate of biodegradation for RC films

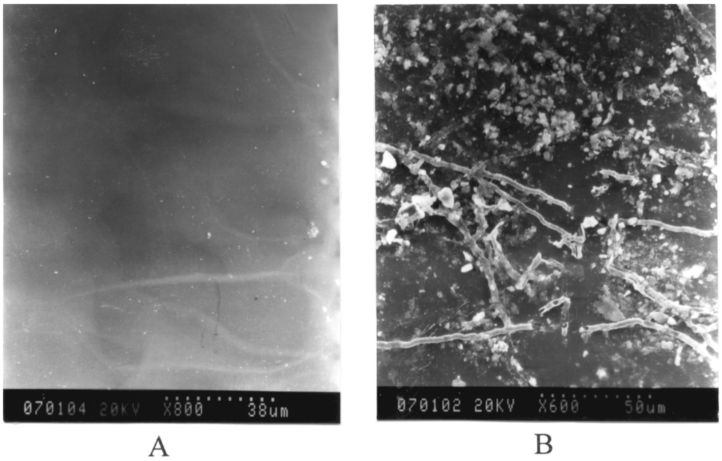

**Figure 7.** SEM photographs of the C-UM$_3$ film before (A) and after (B) biodegradation.

was higher than that for C-UM$_0$, C-UM$_3$, and C-UM$_6$, indicating the coating could inhibit the biodegradation rate. The film C-UM$_0$ was more readily biodegradation than the C-UM$_3$, and C-UM$_6$ films, suggesting the introduction of methyl acrylate to the coating was disadvantage for the enzyme of microorganism degradation the coating. The detail biodegradation mechanism of these films would be reported later.

## CONCLUSION

The composite films were satisfactorily prepared by coating the PU/PMA IPN coating onto the surface of the RC films. The covalent and hydrogen bonds between the RC film and the coating caused strong interfacial bonding, which resulted in excellent mechanical properties in dry and wet state, water resistance, and transmittance. The PU prepolymer in the coating play an important role in forming not only the IPN structure of the coating layer, but also the shared network crosslinked with the cellulose in RC film and copolymer between castor oil and methyl acrylate in the coating. The certain content (20-30 wt%) of methyl acrylate in the coating is disadvantage in biodegradability of the films, but beneficial to improving the water resistance, which is very important to promise the wide application of RC film.

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