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WATER-RESISTANT CELLULOSE FILMS COATED WITH POLYURETHANE-ACRYLAMIDE GRAFTED KONJAC GLUCOMANNAN

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ABSTRACT

The water-soluble coating, including the semi-interpenetrating polymer networks (IPNs) formed by polyurethane (PU) with acrylamide grafted konjac glucomannan (KGM), was prepared and coated to the regenerated cellulose film that was prepared from 7 wt.-% ramie cellulose cuoxam to give water-resistant films. The structure and properties of the coated films were studied by infrared, differential thermal analysis, transmission electron microscopy, ultraviolet, and tensile strength test. It was shown that there was strong interaction between the regenerated cellulose (RC) film and the semi-IPN coating layer at the interface, where covalent bonds and hydrogen bonds formed between –NCO groups in the coating and –OH groups in the RC film. The tensile strength and water resistances evaluated from the mechanical parameters of the coated films were much higher than those of the uncoated films.

Key Words: Acrylamide grafted konjac glucomannan; Konjac glucomannan; Polyurethane; Regenerated cellulose films; Semiinterpenetrating polymer networks; Water resistance

INTRODUCTION

In past decades, with the gradual worsening of a resource crisis, renewable resource has drawn more and more attention due to its promising future of substituting

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for some petrochemical products. As a kind of environmentally friendly material, cellulose films play an important role in packing, separating, exchanging, mulching, and other functional material regions (1). However, the lack of water resistance, due to the three hydroxyl groups in the repeating units of cellulose, limits its wide application. In our former work, water-resistant cellulose films were prepared by coating castor oil-based PU-nitrocellulose (2) and PU-poly (methylacrylate-*co*-styrene) (3) IPNs coatings to the RC cellulose films, respectively. The improvement of water resistance was attributed to the formation of the coshared IPN or semi-IPN structures through the PU prepolymer with cellulose at the interface between the coating and the film, where new covalent and hydrogen bonds occurred. It was reported (4) that compatible cellulose IPNs could be prepared from cinnamate substituted cellulose derivatives with common crosslinked vinyl monomer, and this cellulose film showed high strength. Interestingly, polyurethane block copolymers based on cellulose derivatives (5) and lignin (6) were biodegradable. It is confirmed that -OH groups of some natural polymers can also play the role of polyols in the reaction with -NCO groups. In the latest article (7), IPNs from castor oil-based PU prepolymer and highly deacetylated chitosan were synthesized, showing that the IPNs resulted from the chitosan grafting and crosslinking with PU. RC cellulose films-coated with this IPNs coating had an enhancement of water resistance and tensile strength.

And studies verified that chitosan in the PU-chitosan coating plays an important role not only in accelerating the cure of the coating, but also in improving the biodegradability of the coated films (8). Konjac glucomannan (KGM), a polysaccharide whose main chain is composed of β -1, 4-pyranoside bond linked mannose and glucose (9), has long been used as healthy food in China and Japan. KGM had wide applications to the food and chemical industry, and biochemistry (10–12).

In this work, the PU-AKGM semiinterpenetrating polymer networks (semi-IPNs) coating was prepared through the reaction between the functional group in both individual polymers, that is, -NCO groups in PU prepolymer and -OH in AKGM. It is worth noting that AKGM only dissolved in water. Accordingly, the method of preparing water-soluble PU coating was used here. The properties and morphological structure of the RC films coated with the PU-AKGM coating were studied by using infrared (IR), differential thermal analysis (DTA), ultraviolet (UV), and transmission electron microscopy (TEM). The water resistance and mechanical properties of the coated films were evaluated.

EXPERIMENTAL

Materials and Pretreatment

KGM was extracted and purified according to a previous work (13). Toluene diisocyanate (TDI) (C.P.) was redistilled under reduced pressure before used to remove water. Acetone, butanone, polyethylene glycol (PEG)-600, alcohol, 1,4-butanediol, diethylenetriamine (purchased from Shanghai Chemical Agent Supplier), and sodium hydrogen sulfite were all analytical reagents.



Preparation of AKGM

Two g konjac glucomannan and a 50 mL mixture of alcohol/water (1:1 by volume) were added into an Erlenmeyer flask. Acrylamide (1.6 g) was added into the system and stirred to make it dissolve. The oxygen was excluded under reduced pressure with a water pump for approximately 30 min and then filled with nitrogen. This operation was repeated three times and then injected with a 20-mL cerium ammonium nitrate solution (prepared by dissolved 0.2 g cerium ammonium nitrate in 20 mL 1 mol/L HNO_3). The flask was put in an oscillating reactor, and the temperature was kept at 35°C for 4 h. The crude grafting product was dissolved with enough water by vigorous stirring. Then, acetone was added with moderate stirring and cooling water. The precipitate obtained was again dissolved with water. The operation of dissolving and precipitate was repeated at least three times. After drying the final precipitate at 40°C in vacuum for 8 h, the 2.6-g white powder weighted was obtained. Percent grafting was calculated to be 30% (14). The viscosity-average molecular weight (M_η) of AKGM measured according to $[\eta] = 6.37 \times 10^{-4} M^{0.74}$ at 30°C (15) was approximately 4.06×10^5 .

Preparation of PU-AKGM Semi-IPNs Coating

A four-necked flask was fitted with a nitrogen inlet tube, stirrer, and two pressure-equalizing dropping funnels. PEG (30 g) was poured into one dropping funnel. AKGM (3 g) was dissolved in water to a concentration of 5.5 wt.-%. Where adequate alkali was added to facilitate dissolving. This solution was poured into another dropping funnel. TDI-10-mL butanone (26.1 g) was introduced into the flask, and then PEG was added and mixed with TDI by stirring and under nitrogen atmosphere. The dropping was controlled within 30 min, subsequently, keeping the stirring at the temperature of 60°C for 1 h. Then, 11 g of NaHSO_3 dissolved in water preheated to 50°C was added. After stirring moderately for 30 min, the AKGM solution was added. 10 min stirring at 25°C later, the mixtures of 10 mL acetone-9 g 1,4-butanediol, and 10 mL acetone-6.5 g diethylenetriamine were added sequentially. The chain-extending reaction was controlled at 40°C for 20 min. Finally, adequate glacial acetic acid was added to adjust the pH value of the coating thus obtained to approximately pH = 8. Adequate water was added to adjust the viscosity. The content of solid component was ca. 4%.

Film Preparation

RC Film

Ramie supplied by Hubei Xianning Textile Mill of China was extracted by aceditin for 48 h. Cellulose cuoxam (7 wt.-%) of ramie was prepared according to reference 16 and then cast on a glass plate, and the thickness was controlled as



0.3 mm. The glass plate was dipped into a 10 wt.-% NaOH aqueous solution, and 4 wt.-% H₂SO₄ aqueous solution for 2 min, respectively, then washed in running water and dried at room temperature without additional plasticization. After 8 h, the film was scraped with a blade.

Coated Films

The semi-IPNs coating was coated onto the both sides of the RC films, then cured at 50°C for 12 h. A series of coated films coded as UAKRC-1, UAKRC-2, UAKRC-3, and UAKRC-4 correspond to the cure time for 1, 3, 5, and 8 h, respectively. The uncoated RC film was coded as RC-0. The PU-AKGM film was obtained by casting the coating on a polytetrafluoroethylene plate, then drying at 80°C for 8 h.

Characterization of Films

IR spectra of the films were recorded with a Nicolet 170SX FTIR spectrometer. DTA was conducted using a Thermal Analyzer DT-40 (Shimadzu Co.). The films were cut to 1-mm² size, and the operation was under nitrogen atmosphere from 25 to 500°C at a heating rate of 15°C/min. TEM was performed using a JEM 100-XT electron microscope at 100 kV. Before operation, the films were stained in the vapor of osmium tetroxide for 72 h, then embedded in Epson resin 812. Ultrathin sections were obtained by sectioning on LKB-8800 Ultratome, then stained again in uranyl acetate, and the magnification was ×14000.

Measurements of Properties

Tensile strength (σ_b) and breaking elongation (ε_b) of the films in dry and wet states, which was soaked in water for 1 h before testing, were measured on an electronic strength tester AG-A (Shimadzu Co.) according to the Chinese Standard method (GB4456-84). The water resistance (R) of the films was evaluated from the ratio of σ_b in the wet state [$\sigma_b(\text{wet})$] and σ_b in the dry state [$\sigma_b(\text{dry})$] as follow:

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

The percent light transmittance of the films in the wavelength of 200–800 nm was measured using a UV-160A Spectroscope (Shimadzu, Japan).

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of KGM and AKGM. The two absorption bands around 3100 cm⁻¹ and 3300 cm⁻¹ that is assigned to the stretching of N–H bonds



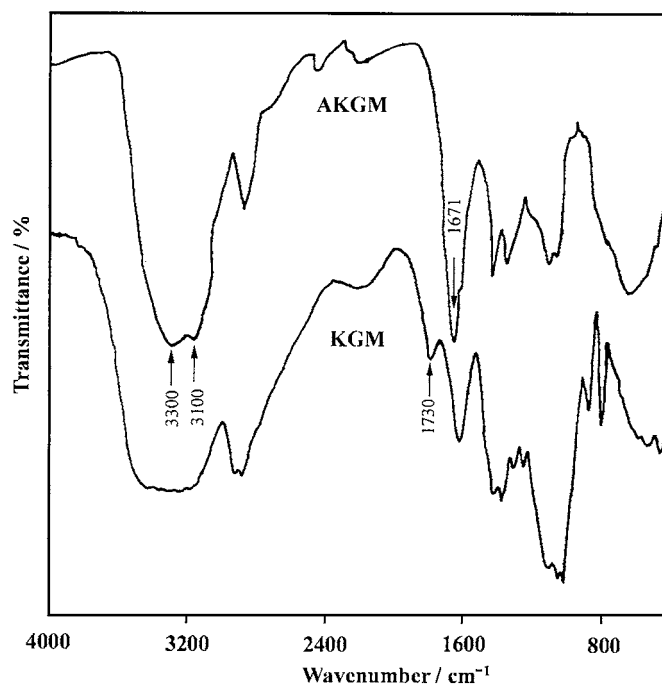


Figure 1. FTIR spectra of the film samples of KGM and AKGM.

appeared in the spectrum of AKGM, and the stretching peak of carbonyl groups at 1730 cm^{-1} that is assigned to the aceto groups in KGM (17) has disappeared for AKGM. Furthermore, a new absorption peak has appeared at 1671 cm^{-1} (18), which is attributed to the combined state carbonyl group of acrylamide, confirming the acrylamide has been grafted to the chains of KGM. All the above evidence has justified the graft modification of KGM by acrylamide. According to the method reported by Cheng (19), the graft efficiency figured out to be 33%.

Figure 2 shows the IR spectra of the uncoated film of RC-0, the coated film of UAKRC-4, and the coating. For UAKRC-4, a new absorption band has appeared at 2856 cm^{-1} , which is attributed to the symmetric stretching of methylene group for the semi-IPN coating. At the same time, the absorption band at 1636 cm^{-1} , which is the special absorption band of the intraester bond of cellulose that can be seen from the spectrum of RC-0, has disappeared in the spectrum of UAKRC-4. A sharp absorption band has appeared at 1650 cm^{-1} in the spectra of UAKRC-4 that is absent in both spectra of RC-0 and the coating, which is attributed to the ester bonds (20) formed by the reaction of the excessive isocyanate groups in TDI and the hydroxyl groups in cellulose. It is suggested that the molecules of the PU prepolymer of PU/AKGM had penetrated into the cellulose. As a result, the esterification had taken place. Further evidence for the occurrence of esterification was the absorption band of UAKRC-4 at 1541 cm^{-1} , which is attributed to the stretching of C–N bond, and further confirms the occurrence of penetration. In addition, the stretching band



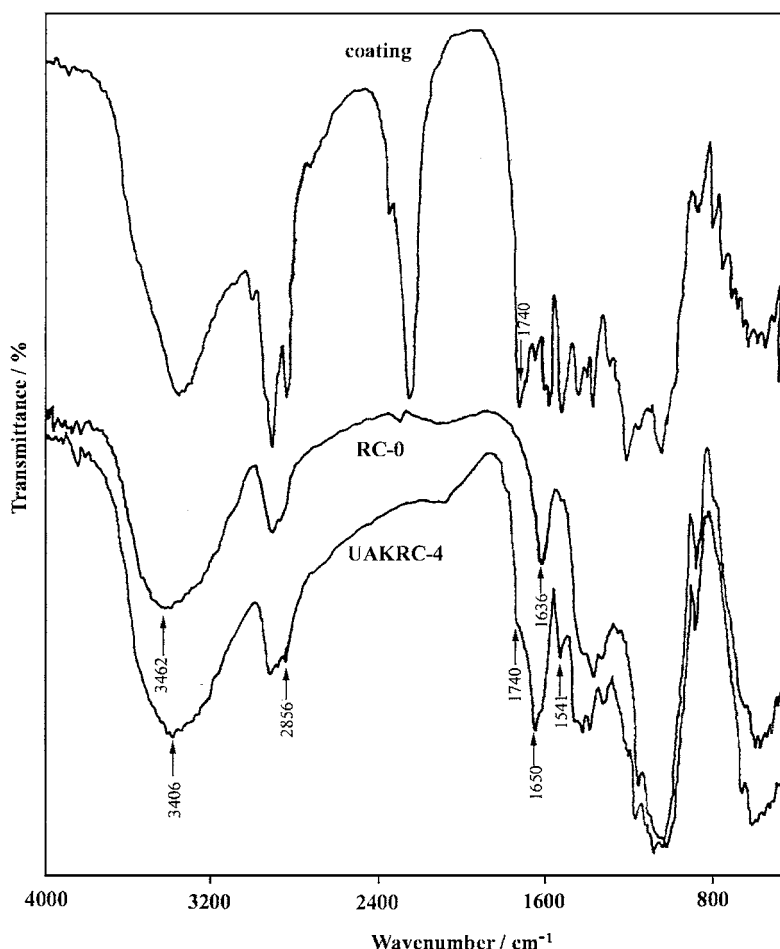


Figure 2. FTIR spectra of the film samples of UAKRC-4, RC-0, and the coating.

of hydroxyl groups at 3462 cm^{-1} , in the spectrum of RC-0, has shifted to a lower wavenumber, that is, 3406 cm^{-1} in the spectrum of coated film UAKRC-4. It indicated the formation of new hydrogen bonds between the coating and RC films in the coated film. The obvious absorption band around 1740 cm^{-1} for the coating, which is assigned to free carbonyls in polyurethane (21), has become a shoulder peak in the spectrum of the film UAKRC-4. According to the studies of Luo et al. and Born et al. (22,23) on the carbonyl region in Fourier transform infrared spectra of polyurethane, this change indicated that the free carbonyls had participated in the formation of hydrogen bonding. Therefore, the carbonyls in urethane, with the penetrating of PU prepolymer molecules, have bonded with -OH groups in RC film through hydrogen bonds.

The DTA thermograms of the films of RC-0, coated films of UAKRC-2, UAKRC-4, acrylamide grafted KGM, and the coating are shown in Figure 3. For



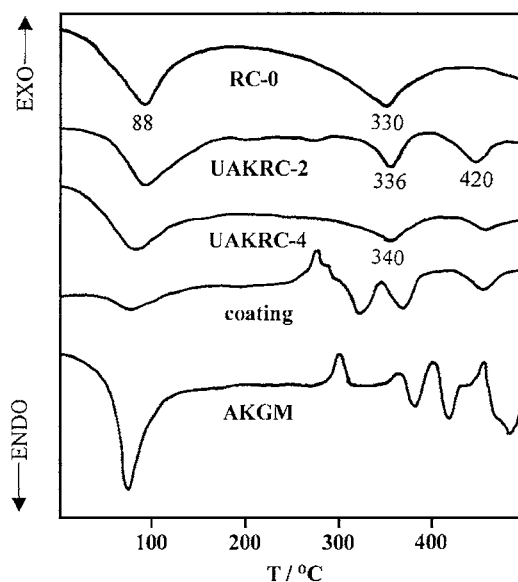


Figure 3. DTA thermograms of film RC-0, coated films of UAKRC-2 and UAKRC-4, and AKGM.

RC-0 there were two endothermic peaks at approximately 88°C and 330°C. The former possibly resulted from partial breakdown of the intermolecular and intramolecular hydrogen bonds, and the latter was due to the complete degradation of cellulose by the breakdown of the pyranosic rings. The exothermic peak appeared at approximately 250–300°C and was assigned to the introduction of KGM. For the coated films of UAKRC-2 and UAKRC-4, the endothermic peak corresponding to the temperature of complete degradation of cellulose, has shifted to 336°C (UAKRC-2) and 340°C (UAKRC-4), respectively, indicating better thermal stability than the uncoated film. In contrast to the thermogram RC-0, a new endothermic peak has appeared at ~420°C, which may be assigned to the semi-IPNs coating. All this evidence from DTA also confirmed the occurrence of the new covalent bonds between the semi-IPN coatings and RC films.

The optical transmittancy dependence of the wavelength (200–800 nm) for the films is shown in Figure 4. The best optical transmission of the film UAKRC-4 at visible wavelengths (400–800 nm) could be observed, suggesting the strong interfacial interaction from hydrogen and covalent bonding between the RC film and coating. However, the UAKRC-1 and UAKRC-2 films corresponding to less than 5 h for the cure time, showed a sharp decrease in optical transmission, where the quantity of light was scattered and reflected at the interface because of the occurrence of interface separation (24).

Figure 5 shows TEM photographs of the section of the film UAKRC-4. The dark region of film indicated a PU-AKGM coating layer 1.1 μm deep. The bottom was cellulose bulk. The coating layer of UAKRC-4 film displays a dark black boundary region ~0.2 μm deep. It can be explained that PU prepolymer molecules



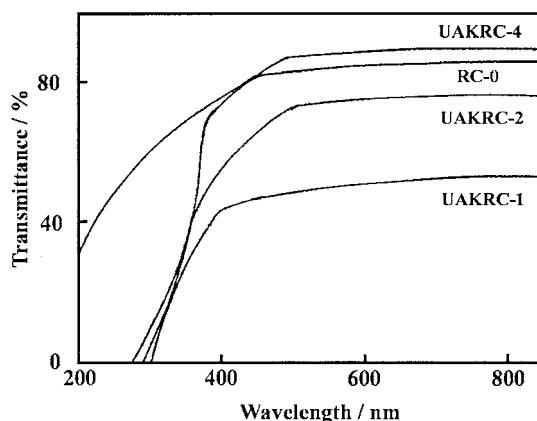


Figure 4. The optical transmittancy dependence of the wavelength for the films.

formed before chain extending in the coating layer much more readily penetrating into the RC film than into the PU molecules. This is because the former has a lower molecular weight and higher content of hydrophilic component. Compared with a previous work concerning the interfacial structure of PU-P (MA-St) coating to RC films in our laboratory, the penetrating depth of PU prepolymer of PU-AKGM was slightly broader. This may be due to the good hydrophilicity of AKGM introduced into the semi-IPNs coating.

There are still disputes on the interfacial adhesion between two substrates (25). Based upon the above analysis results and the diffusion model (26), the strong interfacial interaction between RC film and PU-AKGM coating is considered to be due to the formation of covalent and hydrogen bonds.

The tensile strengths (σ_b), breaking elongation (ε_b), and water resistances (R) of the films are shown in Table 1. It is obvious that the tensile strengths and breaking elongation of RC films in dry state was improved by coating with the

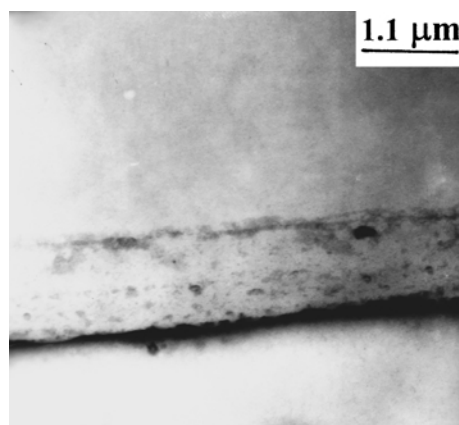


Figure 5. TEM photograph of UAKRC-4.



Table 1. The Tensile Strengths (σ_b , Breaking Elongations (ϵ_b) and Water Resistances (R) of the Films

Film No.	σ_b (MPa)		ϵ_b (%)		R
	Dry	Wet	Dry	Wet	
RC-0	55.9	17.6	21	70	0.31
UAKRC-1	65.2	29.1	36	44	0.45
UAKRC-2	68.8	33.0	23	49	0.48
UAKRC-3	69.0	33.4	28	46	0.48
UAKRC-4	67.4	31.6	31	46	0.47

IPNs coating and curing at a proper temperature. The maximum values of σ_b and ϵ_b reached 69 MPa and 36%. More importantly, the value of σ_b in the wet state was also improved, and the values of water resistance (R) were strongly enhanced. The improvement of mechanical properties and enhancement of the coated films reflected the intimate interaction between the coating and the RC film. These results supported the conclusion drawn from the interfacial structure analysis.

CONCLUSION

The water-soluble PU-AKGM semi-IPNs was prepared by the reaction of TDI with PEG and AGKM and coated onto the RC films. This coated film has excellent tensile strength and water resistance, as well as high optical transmission. Results from interfacial structure indicated that the strong interfacial interaction resulted from the formation of covalent and hydrogen bonding between PU in the coating and the RC film. The obvious penetrating region of PU prepolymer was observed. The interfacial structure of the coated film is interpreted as a coshared polymer network formed by the PU with RC films.

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