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Structure and Properties of Cellulose Films Coated with Polyurethane/Benzyl Starch Semi-IPN Coating

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A series of water-resistant cellulose films was prepared by coating castor oil based polyurethane (PU)/benzyl starch (BS) semi-interpenetrating polymer networks (semi-IPN). All of the coated films, with a very thin coating layer of about 0.4 μm, exhibited much better optical transmittance, water resistance, and mechanical properties than the original regenerated cellulose (RC) film, suggesting a strong interface interaction between PU/BS coating and cellulose substrate. The BS concentration in the coating had a significant effect on the properties of the coated films. With an increase of BS concentration in the coating from 10 to 70 wt %, the tensile strength and storage modulus of the coated films increased. Especially, as the tensile strength achieved a maximum value of 102 MPa, the elongation at break of the coated film still maintained a relatively higher value of 10%. Meanwhile, the coated films displayed good biodegradability, and the biodegradation rate increased with increasing BS concentration in the semi-IPN coating. Therefore, the BS component in the PU/BS coating plays an important role in the simultaneous enhancement of physical properties and biodegradability of the coated films. The good water-resistance character of the coated films could effectively extend the applying area for cellulose.

1. Introduction

The market of petroleum-based polymer materials will be limited because of its inevitable increase in price and severe environmental pollution caused by nondegradability in the future.[1,2] Hence, the research and development of renewable resources including cellulose,[3] starch,[4] and protein[5] have already received much attention because of their biodegradability and potential to substitute for some petrochemical materials. Cellulose, the most abundant natural polymer on the earth, has been reevaluated as a functional material to meet the diverse needs of today's society because of the unique reactivity of molecules.[6,7] However, the application of cellulose products is limited by the sensitivity to water in view of the three hydroxyl groups in the repeat units of cellulose molecule. Many techniques have been provided to improve the water resistance of cellulose so far, where coating is a simple and effective method. Some available water-resistant coatings, such as chitosan/cellulose powder coating,[8] polylactic acid and its derivatives,[9] and nitrocellulose coating,[10] have been explored. For instance, cellophane with relatively poor moisture barrier property is often coated using nitrocellulose wax (NCW) or polyvinylidene chloride (PVDC). Unfortunately, the coating layer either NCW or PVDC can be easily peeled off after soaking in the water for about 5 min.[11,12]

Interpenetrating polymer networks (IPNs) are specific kinds of polymer blends involving cross-linked polymers, which can promote the miscibility between components. The IPN is evaluated as an effective approach to get better properties than either original polymer. We have had a great interest in the development of a castor-oil based polyurethane (PU)/natural polymer derivatives semi-IPN coating, such as PU/nitrocellulose,[12,13] PU/nitrochitosan,[14] PU/benzyl konjac glucomannan,[15] and PU/benzoyl konjac glucomannan,[16] for many years. The regenerated cellulose films (RC) coated with these applications exhibit good water resistivity, mechanical properties, and optical transmittance. It has been explained that the PU-based semi-

IPN coatings possess a good adhesive capability because of the reaction of the excessive −NCO of PU with −OH of cellulose, resulting in a formation of a shared PU network on the interface.[17,18] However, except for benzyl konjac glucomannan, the concentration of other polysaccharide derivatives in the semi-IPN coating should be below 30 wt % for preventing the appearance of severe phases separation.[15] An increasing natural polymers concentration in the blends is essential for a successfully utilized renewable resource. Now, the relatively high price of materials from renewable resource is one of the fatal factors competing with those of petroleum. Therefore, it is very important to search for a natural polymer not only having good miscibility with PU but being much cheaper than konjac glucomannan as well.

In previous work,[19] we have synthesized a benzyl starch (BS) by reacting benzyl chloride with starch and then blended it with PU to prepare semi-IPN materials. Interestingly, the semi-IPN materials are miscible when BS concentration ranges from 5 up to 70 wt %. Moreover, the PU/BS semi-IPN materials with relatively lower molecular weight (M_w) have better miscibility and mechanical properties.[20] In this work, therefore, we attempted to prepare a coating using castor oil-based PU and low molecular BS and then coated them on the RC films to obtain water-resistant films. Simultaneously, the effects of BS concentration in the coating on interfacial structure, thermal stability, water resistance, mechanical properties, and biodegradability of the coated films were investigated.

2. Experimental Section

2.1. Materials. The cellulose (cotton linter pulp) was kindly provided by Hubei Chemical Fiber Group Ltd. of China, and its viscosity-average molecular weight (M_η) was determined to be 1.0×10^5 by viscometer according to $[\eta] = 3.85 M_w^{0.76}$ mL g^{-1} in cadoxen at 25 °C.[21] 4,4′-Diphenylmethane diisocynate (MDI) was purchased from Aldrich Co. (Milwaukee, WI) and used as received. Cornstarch was purchased from Wuhan Starch Co. (Wuhan, China) and consisted of 75% amylopectin and 25% amylose. Other reagents and solvents were all obtained from commercial sources in China. The castor oil was dried at 110

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°C under 20 mmHg for 2 h, and *N,N*-dimethylformamide (DMF) was dried over molecular sieves (4 Å) for 1 week before use, respectively. The benzyl starch (BS) was prepared according to our previous work.[20] The degree of substitution (DS) of BS was calculated to be 0.88 from the data obtained by using an elemental analyzer (CHN-O-RAPID, Heraeus Co., Hanqu, Germany). Weight-average molecular weight (M_w) of BS was determined to be 5.7×10^5 with Debye plots by using a multiangle laser light scattering (MALLS) photometer equipped with a He−Ne laser ($\lambda = 633$ nm; DAMN-DSP, Wyatt Technology Co., Santa Barbara, CA).

2.2. Preparation of Coated Films. Cellulose was dissolved in 7 wt % NaOH/12 wt % urea aqueous solution precooled to be −10 °C, to obtain a transparent cellulose solution with a concentration of 4 wt %. The cellulose solution was poured into a glass plate and was immediately immersed into 5 wt % H_2SO_4 aqueous solution for 5 min.[22,23] The resultant wet films were washed with running water and then air-dried at ambient temperature to obtain the dry RC films with a thickness of about 40 μm.

PU prepolymer ([NCO]/[OH] = 2) was synthesized as described in another article.[20] The PU prepolymer and the desired mass of BS were dissolved in DMF, respectively, and then were mixed to yield a coating with a solid content of about 2 wt %. Then, the RC films were dipped into the coating solution and were taken out after 10 s to cure at 60 °C for 5 min to obtain the coated films. It worth noted that the coated film without BS in the coating should be cured at 60 °C for 80 min; this suggests that the addition of BS can accelerate the cure process of the semi-IPN coating. The coated RC films were coded as CUB0, CUB10, CUB20, CUB30, CUB40, CUB50, CUB60, and CUB70, respectively, according to the BS concentration increased from 0 to 70 wt % in the coating. The films were vacuum-dried at room temperature for 3 days before characterizations.

2.3. Characterization. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) of the films was performed on a spectrometer (1600, Perkin-Elmer Co., Norwalk, CT). The samples were taken at random from the flat films, and the data were collected over 32 scans with a resolution of 4 cm^{-1} at room temperature. Transmission electron microscopy (TEM) analysis was carried out on a transmission electron microscope (TECNAI G^{2}20, FEI Co., Hillsboro, OR) at an accelerated voltage of 200 kV. The sample preparation was based on the Kato's osmium tetroxide staining technique.[24] The CUB20 film was stained in a vapor of osmium tetroxide at room temperature for 1 week and then was embedded in an opoxy resin. Ultrathin sections of the sample were prepared using a Leica Ultracut UCT with EMFCS cryoattachment at −120 °C. The percent optical transmittance (*Tr*) of the films was measured by using an ultraviolet−visible spectrophotometer (UV-160A, Shimadzu, Japan) at 800 nm.

Thermogravimetric analysis (TGA) curves of the RC and coated films were recorded on a STA 499C thermoanalyzer (Netzsch, Waldkraiburg, Germany) under nitrogen atmosphere from 20 to 600 °C at a heating rate of 10 °C min^{-1}. Dynamic mechanical thermal analysis (DMTA) was carried out on a DMTA-V dynamic mechanical thermal analyzer (Rheometric Scientific Co.) at a frequency of 1 Hz in the temperature range from −120 to 320 °C with a heating rate of 5 °C min^{-1}. The specimens with typical size of 10 mm × 10 mm (length × width) were used.

The tensile strength (σ_b) and elongation at break (ϵ_b) of the films were measured on a universal testing machine (CMT 6503,

Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) according to ISO standard 527-3:1995(E) at room temperature with a crosshead speed of 5 mm min^{-1}. An average value of at least five replicates for each sample was taken. Prior to the test, the samples were kept in the atmosphere of 75% relative humidity for 2 weeks to ensure the equilibration of the water content in the films. To obtain the $\sigma_{b(wet)}$ values for the films in wet state, the films were soaked in water for 10 h before testing. The water resistivity (R_σ) of the films was evaluated from the values of $\sigma_{b(dry)}$ in the dry state and $\sigma_{b(wet)}$ in the wet state as

$$R_\sigma = \sigma_{b(wet)}/\sigma_{b(dry)} \tag{1}$$

The value of contact angle of water droplet on the RC and CUB films in air was evaluated from images of the drop profile, which were monitored as a function of time by a DSA 10 instrument (Kruss, Hamburg, Germany). The droplet volume was about of 10 μL, and triplicate measurements yielded a variation of ±1°.

2.4. Biodegradation Test. Natural soil was used as the biodegradation environment. The CUB20 film (8 × 8 cm^2) was enclosed separately in nylon meshes and buried about 15 cm beneath the soil in Wuhan University campus. The average values of the temperature, air moisture, and pH of the soil were measured to be 30 °C, 65%, and 6.8, respectively. From 7 to 40 days after being buried, the degraded films and fragments were taken out one after another, rinsed carefully with distilled water, and then vacuum-dried at room temperature. Surfaces of the degraded films were observed by a scanning electron microscope (SEM, Hitachi S-570 microscope, Tokyo, Japan) at 20 kV after being coated with gold.

During the degradation of the films, the released carbon dioxide was monitored according to the ISO 14852:1999(E) with some modifications. *Fusarium moniliforme* (AF 93241), *Chaetomium divaceum* (AF 93119), *Aspergillus oryzae* (AF 93017), and *Trichoderma viride* (AF 93252) were supplied by China Center for Type Culture Collection (CCTCC) of Wuhan University. A mineral salts medium containing (g/L) 0.085 of KH_2PO_4, 0.2175 of K_2HPO_4, 0.334 of $Na_2HPO_4 \cdot 2H_2O$, 0.005 of NH_4Cl, 0.00025 of $FeCl_3 \cdot 6H_2O$, 0.0364 of $CaCl_2 \cdot 2H_2O$, and 0.0225 of $MgSO_4 \cdot 7H_2O$ was used in this study. Then 15 wt % of agar was added to the mineral salts medium, sterilized by autoclaving at 121 °C for 20 min, contained in a Petri plate to provide a solidified agar layer. The CUB20 and CUB80 films were cut into small fragments and placed on the surface of the agar layer respectively, and then the strain pore suspension (0.2 mL/dish, 10^6 pore/mL) was spread on the surface of the fragments. Both the agar plate and beaker containing 40 mL of 0.1 mol/L $Ba(OH)_2$ solution as the CO_2 absorbent were placed in a 2500 mL desiccator. The desiccator was closed and incubated at 28 °C. The CO_2 absorbent was titrated with 0.08 mol/L of oxalic acid. Blanks for these trials were prepared identically except for the film addition. The experimental values of net CO_2 evolution ($CO_{2,EXP}$) were calculated according to the volume of consumed oxalic acid in titration and the blank control. The theoretical values of CO_2 evolution ($CO_{2,THE}$) were calculated by the carbon content (w_c) in the films from element analysis. The extent of biodegradation (R) was given as

$$R = (CO_{2,EXP}/CO_{2,THE}) \times 100\% \tag{2}$$

3. Results and Discussion

3.1. Structure of Coated Films. The ATR-FTIR spectra of the PU and CUB20 films are shown in Figure 1. The PU film exhibits the characteristic absorption peak of free N=C=O group at 2274 cm^{-1}, whereas the peak at the same wavenumber
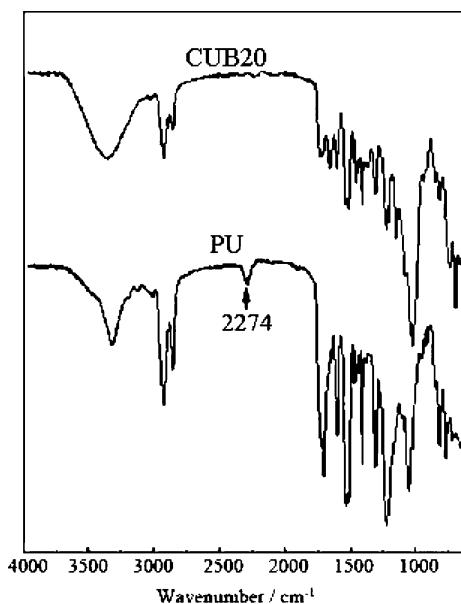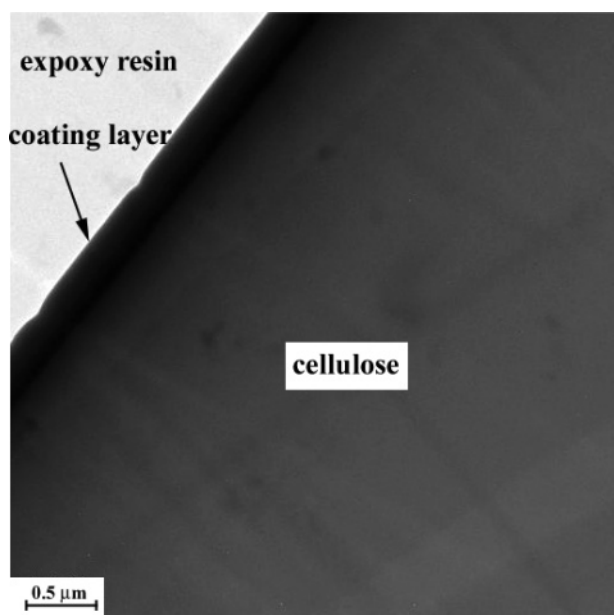
Figure 1. ATR-FTIR spectra of PU and CUB20.

Figure 2. TEM image of the cross section for the CUB20 film.

disappears in the spectrum of the CUB20 film. This can be explained by the fact that the excess −NCO groups of PU prepolymer molecules on the coated films have reacted with both COH of BS in the coating layer and −OH of cellulose. In this case, the PU/BS coating penetrated into the RC film and the reaction of PU prepolymer with BS in the coating and −OH groups of cellulose occurred simultaneously, accompanying with the pervasion of DMF solvent during the coating process. Thus, shared PU networks have occurred between the coating and the RC film in the curing process.[12] Figure 2 shows the TEM image of the CUB20 film. The dark domain of about 0.4 μm wide in the middle is the PU/BS coating layer, and the top in undertone and the bottom in gray are the epoxy resin and cellulose substrate, respectively. A misty transition boundary region can be observed between the coating layer and the cellulose substrate. This indicates directly that the semi-IPN coating can penetrate easily into the RC film with porosity because of its low viscosity and good fluidity. Moreover, there are no flaws are observed at the interface; this demonstrates that a tight
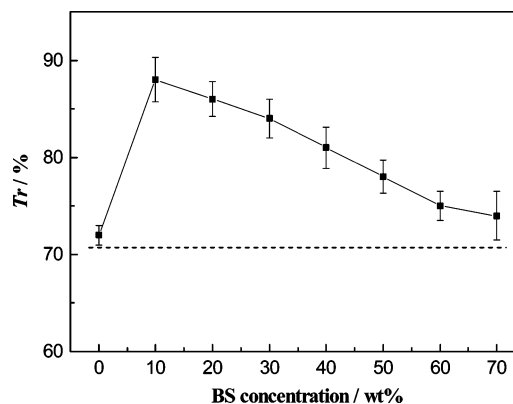

Figure 3. Dependence of optical transmittance (*Tr*) at 800 nm on the BS concentration for the coated films. (---- represents the *Tr* of the RC film.)

adhesion has formed as a result of the reaction between −NCO of PU prepolymer and the −OH of the cellulose.

The optical transparency (*Tr*) of the films is an auxiliary criterion to judge the miscibility of the composites. The dependence of *Tr* at 800 nm on BS concentration for the CUB films is shown in Figure 3. It is worth noting that the *Tr* values of all coated films are higher than that of the RC film. Usually, the interface between two dissimilar materials will cause a loss of optical transmission, because the light will be scattered and reflected at the interface between the different solid materials. The enhancement of the *Tr* value of the coated films is mainly ascribed to a much smooth surface of the coated film and a tight adhesion in terms of strong interface interaction between the coating layer and the cellulose substrate. The *Tr* of the CUB0 film without BS in the coating layer is lower than those of coated films but higher than that of RC film. This supports that the introduction of BS not only disturbs the ordered microdomain of PU but also forms strong interactions with PU due to the esterification and hydrogen bonding as well. In addition, the *Tr* values of the coated films decrease with an increase of BS concentration from 10 to 70 wt %. It may be attributed to the increase of the degree of phase separation in the coating layer, accompanying with the decrease of the concentration of free −NCO groups.

3.2. Thermal Stability. The thermogravimetric curves (TG/ DTG) for the RC film and the coated films with different BS concentration are shown in Figure 4. All of the films have similar behavior with two main stages of mass loss. The first stage, observed up to about 150 °C, is related to the loss of absorbed and bound water. And the second stage started at ca. 300 °C is mainly assigned to the cellulose decomposition. In a comparison of the thermograms, it is found that the decompositions of coated films, especially the CUB70, start at lower temperature than that of RC film. It is attributed to the decomposition of BS in the coating layer because starch usually has an initial temperature of degradation at about 280 °C which is lower than that of cellulose. However, the temperature at maximum decomposition rate of the coated films is higher than that of the RC (339 °C) film and increases with an increase of the BS concentration in the coating layer. This indicates that some molecules of cellulose have better thermal stability because of the formation of shared networks between the coating and the cellulose, and the addition of BS can improve this kind of effect further.

Figure 5 shows the dependence of storage modulus (*E*′) on temperature for the coated films with different BS concentration and the RC film. The *E*′ values of the coated films are remarkably higher than that of the RC film within the whole
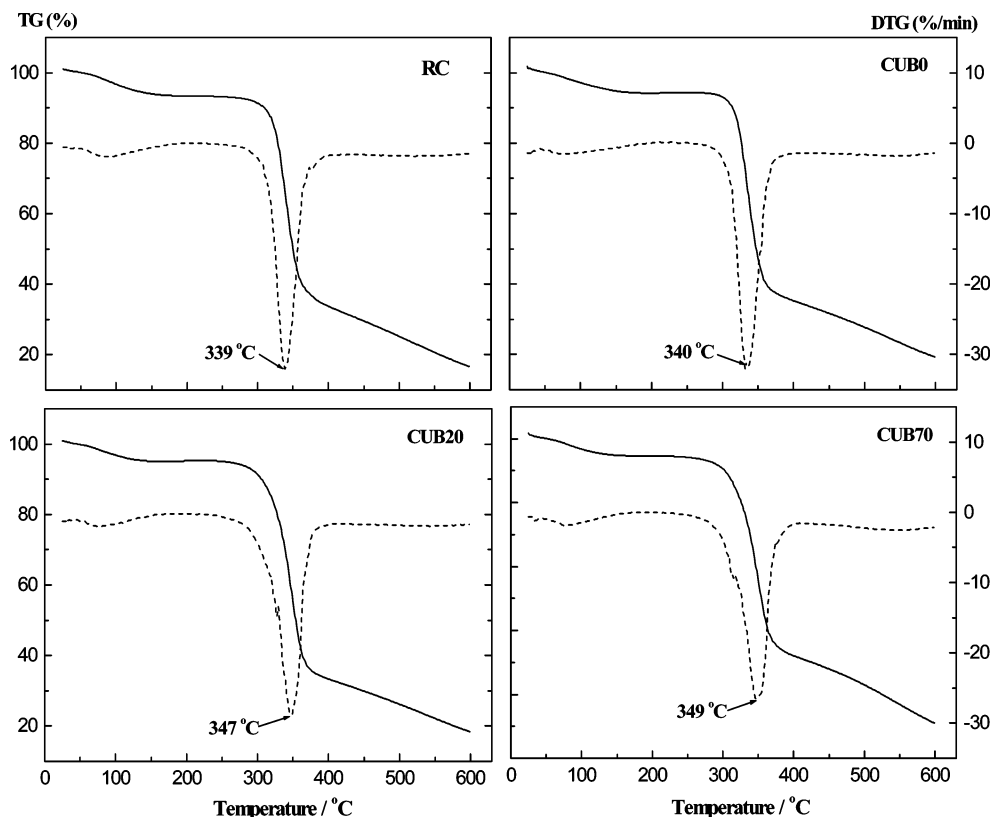
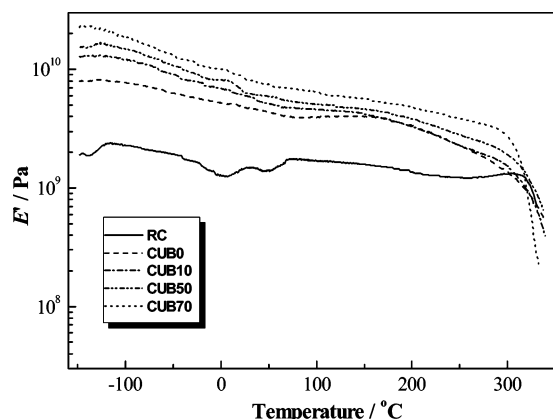**Figure 4.** TG (—) and DTG (---) curves for the RC and coated films.

Figure 5. Dependence of storage modulus (E') on temperature for the RC and coated films.

Figure 6. Dependence of tensile strength (σ_b, ●) and elongation at break (ϵ_b, ○) of the RC and coated films on BS concentration. ---- and ⚊⚊ represent σ_b and ϵ_b of RC film in the dry state, respectively.

temperature range. The gaps of E' values between the RC film and the coated films reach even more than 6×10^9 Pa at room temperature. This can be explained by the fact that the molecules of PU prepolymer penetrate into the cellulose substrate to react with −OH groups in cellulose and therefore form a network, resulting in the greater difficulty of micro-Brownain motion of the cellulose segment in the amorphous region.[15] Moreover, the E' value for the CUB films monotonically increases with the increasing of BS concentration in the coating layer, suggesting the effective reinforcement of the BS for the coated films. The storage modulus decreases gradually until a sharp decrease at about 310 °C, assigned to the thermal decomposition of cellulose. The cellulose film does not exhibit glass−rubber transition before the decomposition because its glass transition temperature is higher than the decomposition temperature as a result of the strong inter- and intramolecular hydrogen bonding. Furthermore, the content of the coating layer is so low that the
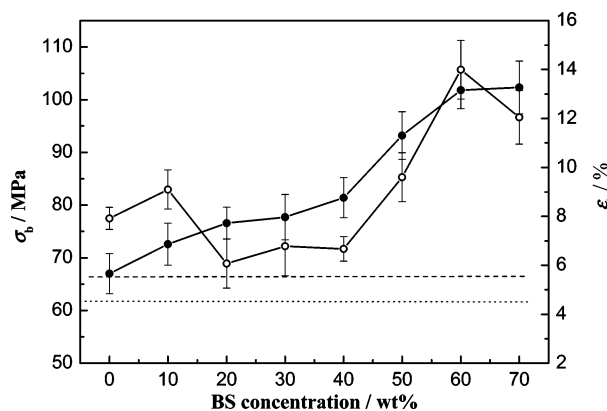
corresponding glass transition of the coating could not be detected in this case.

3.3. Mechanical and Physical Properties of Coated Films. Figure 6 shows the dependence of tensile strength (σ_b) and elongation at break (ϵ_b) on BS concentration in the coating for the coated films in dry state. And the values of σ_b and ϵ_b for the RC film and the coated films both in dry and wet states are listed in Table 1. Compared with the RC film, the coated films possess much higher σ_b at dry state. Interestingly, the σ_b and ϵ_b values of the coated films increase simultaneously with the increasing BS concentration on the whole and reach maximum values of 102 MPa and 14%, respectively, for CUB60. It is mainly attributed to the interpenetration and entanglement of the macromolecular chains, namely shared PU networks, at the interface between coating layer and the cellulose substrate. The strong hydrogen bond between macromolecules and the formation of networks lead to this simultaneous enhancement of σ_b

Table 1. Tensile Strength (σ) and Elongation at Break (ϵ_b) in Dry and Wet States and Water Resistivity (R_σ) for the Coated Films

| samples	$\sigma_{(dry)}$/MPa	$\epsilon_{b(dry)}$/%	$\sigma_{(wet)}$/MPa	$\epsilon_{b(wet)}$/%	R_σ
RC	65.2 ± 2.8	4.4 ± 0.6	15.4 ± 3.1	17.6 ± 1.2	0.24
CUB0	67.0 ± 3.8	7.9 ± 0.4	33.1 ± 2.8	16.3 ± 0.5	0.49
CUB10	72.6 ± 4.0	9.1 ± 0.8	36.9 ± 2.5	17.9 ± 0.9	0.51
CUB20	76.6 ± 3.1	6.1 ± 1.0	40.3 ± 3.2	14.6 ± 1.2	0.53
CUB30	77.7 ± 4.3	6.7 ± 1.2	32.9 ± 4.1	14.4 ± 1.0	0.42
CUB40	81.4 ± 3.8	6.7 ± 0.5	33.6 ± 2.9	20.3 ± 0.9	0.41
CUB50	93.2 ± 4.5	9.6 ± 0.9	47.1 ± 2.8	19.6 ± 1.3	0.50
CUB60	102 ± 3.5	14.0 ± 1.2	42.9 ± 3.6	24.6 ± 2.0	0.42
CUB70	101 ± 5.1	12.0 ± 0.9	35.4 ± 4.3	25.9 ± 1.9	0.35

and ϵ_b of the coated films. It is very important for preparation of materials from that with high content of natural polymer derivative. The R_σ values for the coated films evaluated by the σ_b values are also summarized in Table 1. The R_σ values of the coated films are much higher than that of the RC film; this suggests that the dense hydrophobic coating layer on the surface of cellulose film contributes greatly to the improvement of the water resistivity. Furthermore, the PU/BS coating layer could not be peeled off from the RC film even if the coated films wre dipped in heating water for a long time. This further

confirmed the formation of shared PU networks between the semi-IPN coating and cellulose film. This work resolves the problem of the coating layer could be peeled off easily for NCW or PVDC coated films in water.

Photograph of water drop deposited on the CUB50 film surface is shown in Figure 7. It illustrate that the water has a low affinity for the surface of coated film, which has a relatively high hydrophobicity. Figure 8 shows the dependence of contact angle on BS concentration for the CUB films. The contact angle of the coated films is much higher than that of RC film (64°) and reaches a maximum value of 93° for CUB0. This result further verifies that the coated films have much better water resistivity than RC film. It is noted that the contact angles of the coated films decrease with an increase of the BS concentration in the coating layer. This can be explained that the coating layer with more BS has better hydrophilicity than PU because the BS containing −OH is more hydrophilic than PU. Moreover, the coating with higher PU prepolymer concentration reacts more easily with BS and cellulose, resulting in a coating layer with higher density and better water resistivity. Therefore, this work provides a convenient way to prepare water-resistant cellulose films having good mechanical properties.

3.4. Biodegradability. Figure 9 shows the SEM images of the CUB20 film degraded in the natural soil for different time. The SEM image of CUB20 degraded for over 21 days cannot be obtained because it has been broken into very small fragments and is difficult to be taken out from the soil. A porous structure with fungal mycelia on the surface of the decayed CUB20 film, caused by microorganisms, is observed (Figure 9B,C). It is noted that the surface of the CUB20 film becomes slightly coarse after buried for 7 days and becomes coarser with an increase of the degradation time. This indicates that the coated RC films exhibit good biodegradability.

Figure 10 shows the incubation time dependences of CO_2 evolution for the CUB20 and CUB70 films in the agar medium. Generally, the ratio of CO_2 release of good biodegradable materials is 60−70% and the other carbon is converted to biomass production.[25,26] The extent of biodegradation (R) of the CUB20 and CUB70 films incubated for 44 days is 36% and
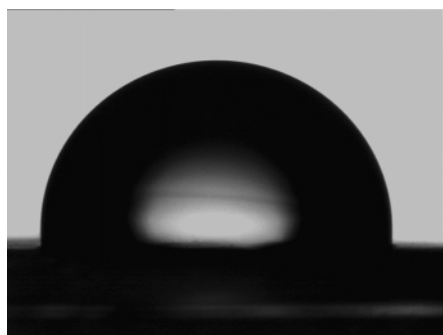
Figure 7. Photographs of a water drop on the CUB50 film surface after 30 s.
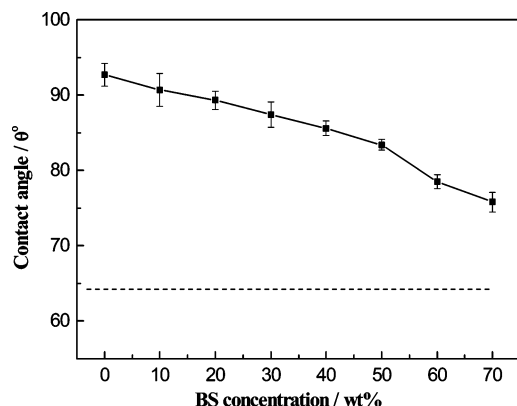
Figure 8. Dependence of contact angle on BS concentration for the coated films. (--- represents the contact angle for the RC film.)
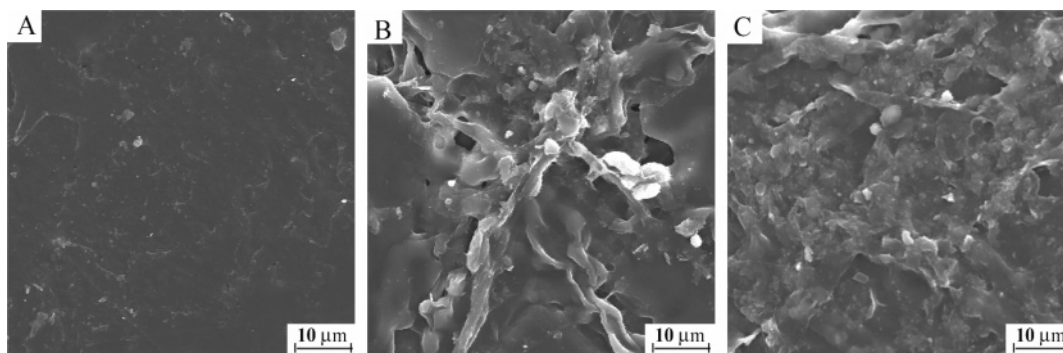
Figure 9. SEM images of the CUB20 coated film decayed in soil for 7 days (A), 14 days (B), and 21 days (C).
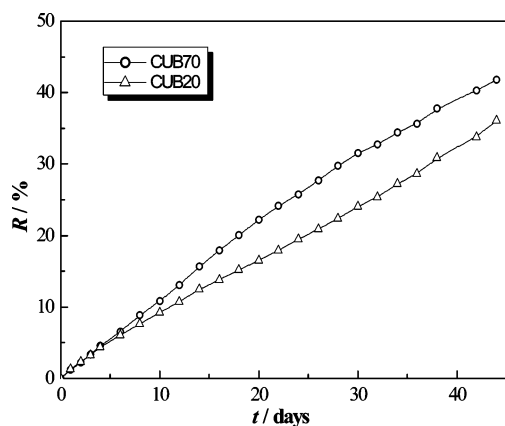
Figure 10. Incubation time dependence of CO_2 evaluation for the CUB20 and CUB70 coated films for 44 days.

42%, respectively, and these values have not reached a plateau. Moreover, the degradation rate of the CUB70 film is obviously faster than that of the CUB20 film, indicating that the biodegradability of the coated films increases with an increase of BS concentration in the coating. In addition, the better water resistivity and the higher density of the coating layer lead to a delay of the degradation of the coated films by fungi. The results above indicate that the microorganism in the soil directly attacked the coating layer of CUB20 film and then penetrated into the cellulose substrate to achieve metabolism, resulting in the CO_2 release from cellulose. It has been reported that, except for the benzyl konjac glucomannan,[27] the natural polymer derivatives in semi-IPN coatings are less than 30 wt %; otherwise, a greater percent will result in serious phase separation and poor mechanical properties.[12,28–29] In view of both environmental conservation and sufficient utilization of renewable resources, the development of an IPN coating containing more natural polymers is very essential for both scientific and applied researches of natural polymers. In this work, the content of starch derivative BS in the coating has achieved 60–70 wt %, and CUB60 exhibits better mechanical properties and biodegradability than others. Therefore, the CUB coated films provide a potential application where the biodegradation is very important.

4. Conclusions

Water-resistant regenerated cellulose films were successfully prepared by coating the castor-oil based PU/benzyl starch semi-IPN with a thickness of 0.4 μm on cellulose substrate. The coated cellulose films exhibited higher water resistivity, optical transmittance, and thermal stability, as well as better mechanical properties in dry and wet states, than the original RC film. The concentration of starch derivative BS in the coating could achieve 60–70 wt %. It was noteworthy that the coated film with 60 wt % BS in the coating possessed the highest tensile strength of 102 MPa and the elongation at break (14%). The coated films are biodegradable; meanwhile, the biodegradation rate increased with the increasing of BS concentration in the coating. Therefore, the BS addition plays an important role in the acceleration of the cure process of the semi-IPN coating, as well as the improvement of mechanical properties and biodegradability of the coated films.

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