

Miscibility and Properties of Blend Materials from Waterborne Polyurethane and Carboxymethyl Konjac Glucomannan

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ABSTRACT: We prepared composite materials by blending waterborne polyurethane (WPU) and carboxymethyl konjac glucomannan (CMKGM) with CMKGM content from 15 to 80 wt % in an aqueous system. The structures and properties of the blend materials were characterized by FTIR, dynamic mechanical analysis, ultraviolet spectroscopy, scanning electron microscopy, wide-angle X-ray diffraction, thermogravimetric analysis, and tensile testing. The results indicated that the blend sheet with 80 wt % CMKGM exhibited good miscibility and higher tensile strength (89.1 MPa) than that of both WPU (3.2 MPa) and CMKGM (56.4 MPa) sheets. Moreover, with an increase of CMKGM content, the tensile strength, Young's modulus, and thermal stability increased significantly, attributed to intermolecular

hydrogen bonding between CMKGM and WPU. Based on the experimental results, the blend materials have good, or a certain degree of, miscibility over the whole range of composition ratio of WPU to CMKGM. In addition, the blend materials exhibited organic solvent resistance. This work not only provided a simple method to prepare environmentally friendly materials, but also expanded the application of CMKGM. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 77–83, 2004

Key words: waterborne polyurethane (WPU); carboxymethyl konjac glucomannan (CMKGM); blends; dynamic mechanical analysis; miscibility

INTRODUCTION

Natural polymers including their derivatives are an emerging field because of their regeneration and excellent biodegradability.¹ Konjac glucomannan (KGM), a natural polysaccharide isolated from the plant tuber of *Amorphophallus Konjac*, is composed of β -mannose and β -glucose in the molar ratio of 1 : 1.6 with a low degree of acetyl groups.² KGM can be used in the fields of food, pharmaceuticals, and chemical engineering. However, the use of KGM as a material is limited because its stability and water resistance are poor. Therefore, we attempted to improve these properties to expand the application of KGM through the use of physical and chemical modification. Blending is a simple and effective method to obtain new materials from both academic and industrial vantage points.³ Moreover, blends of polymers may result in a reduction in the basic cost and an improvement in processing, and also enhance properties.⁴ In our laboratory, physical and chemical properties of the blend materials were improved by blending KGM with other natural polymers, such as cellulose^{5,6} and chitosan.⁷ On

the other hand, chemical modification of KGM was also used to enhance the mechanical properties. For example, water solubility, stability, film-forming ability, and light transmittance of carboxymethyl konjac glucomannan were significantly improved, compared with unmodified KGM.^{8–10}

In an effort to be more environmentally conscious, some changes were implemented to restrict solvent emissions, particularly volatile organic compounds (VOCs).¹¹ It is noted that waterborne polyurethane (WPU), as a nontoxic, nonflammable, and environmentally friendly material, allows a broad range of applications, plastics coating, automatic finishing, industrial finishing, and corrosion-protection coating, for example.^{12–16} WPU has a potential miscibility with carboxymethyl konjac glucomannan (CMKGM) because both have hydrophilic groups. Properties of polymer blends depend mainly on the state of miscibility, which is generally considered the result of specific interactions between polymer segments.¹⁷ Therefore, it is considered that the complex materials composed from WPU and CMKGM can improve their mechanical properties. In this work, we synthesized WPU and CMKGM, respectively, and prepared a series of blend materials by blending WPU and CMKGM in aqueous system. The effect of CMKGM content on miscibility, morphology, thermal stability, tensile strength, and solvent resistance of blend sheets was investigated through the use of FTIR, dynamic

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mechanical analysis (DMA), ultraviolet (UV) spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), tensile testing, and solvent swelling testing, and results were discussed.

EXPERIMENTAL

Materials

KGM was supplied by Zhuxi Konjac Institute (Hubei, China) and was purified according to our previous method.⁷ KGM (5 g) was dissolved in deionized water to prepare a concentration of 1.5 wt %, and then 30 wt % aqueous NaOH (15 g) was poured into the mixture. After being stirred vigorously at room temperature for 1.5 h, the alkali–konjac glucomannan slurry was centrifuged at 5000 rpm for 15 min; the supernatant was transferred to a two-neck flask equipped with mechanical stirrer and pressure-equalizing dropping funnel. The desired chloroacetic acid aqueous solution with a small amount of KI, which could facilitate reaction, was dropped into the flask at 60°C, with continuous stirring at 70°C for 2 h to obtain a clear solution. The solution was then neutralized with 30 wt % hydrochloric acid to a pH of 8–9. The resulting product CMKGM was precipitated with ethanol, washed with 50 and 80 wt % aqueous ethanol two times, and immersed in 98 wt % ethanol overnight. The product was vacuum-dried to obtain the pure CMKGM. The other chemical agents were analytical grade.

Anionic WPU were prepared through a two-stage polymerization process.^{18,19} Commercial 1,4-toluene diisocyanate (TDI; Shanghai Chemical Co., Shanghai, China) was vacuum-dried at 80°C for 2 h and used as hard segments. Polypropylene glycol (PPG, $M_w = 2000$; Shanghai Chemical Factory, Shanghai, China) was vacuum-dried at 105°C for 5 h and used as soft segments. Dimethylol propionic acid (DMPA; Chengdu Polyurethane Co., Chengdu, China) was also dried under vacuum at 110°C for 2 h and used as chain extender and anionic center. Triethylamine (TEA; Shanghai Chemical Co. Shanghai, China) and acetone as neutralized reagent and solvent, respectively, were treated by 3-Å molecular sieves for more than 1 week to dehydrate them before use. The dry PPG (31.5 g) was heated to 75°C with mechanical stirring in a three-neck flask, after which TDI (9.6 g) was added in one portion, and stirring was continued at 75°C for 2 h. Then an equivalent amount of dry DMPA (2.11 g) was added in one portion to the stirred mixture, and the reaction was carried out for 2–3 h until the content of NCO groups reached a given value, as determined by dibutylamine back titration.²⁰ Acetone (40 mL) was added to the resulting product to reduce the viscosity of the prepolymer. Finally, the product was cooled to 50°C, and neutralized with TEA

for 30 min. The WPU was formed by dispersion in deionized water for 30 min. The solid content of the WPU was 9.6%.

Preparation of blend materials

CMKGM (3 g) was dissolved in 150 g deionized water to obtain 2 wt % CMKGM solution. The WPU was mixed with CMKGM solution at room temperature, with continuous stirring for 1.5 h. The mixture was then cast onto a polytetrafluorethylene plate and dried at 50°C for 1 day to obtain the blend sheet. By changing the weight ratio of CMKGM in the blend sheets such as 15, 30, 50, 60, and 80 wt %, a series of blend sheets were prepared, coded as CMPU15, CMPU30, CMPU50, CMPU60, and CMPU80, respectively. The thickness of the blend sheets was in the range of $70 \pm 10 \mu\text{m}$. The sheets from pure CMKGM and WPU were coded as CMKGM and WPU, respectively.

Characterization

IR spectra of the samples were recorded with a FTIR spectrometer (model 1600, Perkin–Elmer Co., Boston, MA). The sheets were cut to 0.5 mm length and 0.5 mm width, vacuum-dried, and then mixed with potassium bromide to laminate. It was difficult for WPU to be cut, so the WPU sheet was performed with attenuated total reflection on the same instrument. The WPU sheet was taken at random on the flat sheet and the data were collected over 16 scans with a resolution of 4 cm^{-1} at room temperature.

DMA was performed with a dynamic mechanical thermal analyzer (DMTA-V; Rheometric Scientific, Piscataway, NJ) at 1 Hz and a heating rate of 5°C min^{-1} in the temperature range from -80 to 200°C . The specimens with typical size of $10 \times 10 \text{ mm}$ (length \times width) were used here.

Optical transmittance (T_r) of the sheets were measured with a UV–vis spectrophotometer (UV-160A, Shimadzu, Kyoto, Japan) at a wavelength of 800 nm, and the thickness of sheets was about $70 \mu\text{m}$.

The SEM images for morphology of the surfaces and cross sections were taken with a scanning electron microscope (X-650 Hitachi, Tokyo, Japan). The sheets were frozen in liquid nitrogen and snapped immediately, after which they were vacuum-dried. The surface and cross section of the sheets were sputtered with gold, observed, and photographed.

Wide-angle X-ray diffraction (WAXD) patterns were recorded on an X-ray diffraction instrument (XRD-6000; Shimadzu, Kyoto, Japan), by Cu– K_α radiation ($\lambda = 15.405 \text{ nm}$) at 40 kV and 30 mA with a scan rate of 4° min^{-1} . The diffraction angle ranged from 5 to 35° .

Tensile strength (σ_b) and elongation at break (ϵ_b) of the sheets were measured on a versatile tester (CMT-

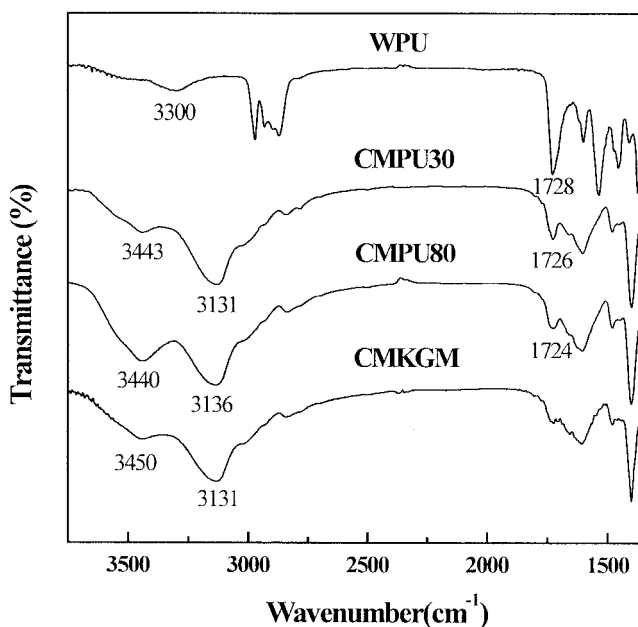


Figure 1 FTIR spectra of WPU, CMKGM, and blend sheets.

6503; Shenzhen SANS Test Machine Co., Shenzhen, China) according to the ISO6239-1986 standard with a tensile rate of 5 mm min^{-1} . The size of the samples was $70 \times 10 \times 50 \text{ mm}$ (length \times width \times distance between two clamps).

TGA thermograms of the specimens with 1 mm width and 1 mm length were recorded on a therm analyzer (DT-40; Shimadzu) under nitrogen atmosphere with a flow capacity of 50 mL/min from 20 to 600°C , at a heating rate of $10^\circ\text{C min}^{-1}$.

Solvent swelling testing of the sheets in different solvents such as ethyl acetate and toluene were carried out as follows. The dry sheets (w_0) [$1 \times 1 \text{ cm}$ (length \times width)] were weighed, placed into 100 mL of the solvent, and immersed from 1 to 24 h at 30°C . The resulting sheets were removed, and the excess solvent on the sheet was wiped off with a paper cloth before weighing. The degree of swelling (W_{sol}) was calculated by the following equation:

$$W_{\text{sol}} (\text{wt } \%) = [(w_s - w_0)/w_0] \times 100\% \quad (1)$$

where w_s represents the weight of the swollen sheet. Three samples were tested to obtain an average value of the degree of swelling.

RESULTS AND DISCUSSION

Miscibility and morphology of blend sheets

Figure 1 shows the FTIR spectra of WPU, CMPU30, CMPU80, and CMKGM. Compared with the spectrum of KGM,⁷ there are some changes in the spectrum of CMKGM: a shoulder peak at 1658 cm^{-1} appeared,

attributed to the carbonyl group, and the absorption band around 3400 cm^{-1} shifted to a higher wavenumber, attributed to $-\text{OH}$ stretching vibration. Introduction of CH_2COO^- into KGM destroyed the original hydrogen bonds in KGM.²¹ Apart from the above, it is obvious that the absorption bands centered at 1607 and 1400 cm^{-1} , which are attributed to asymmetric and symmetric stretching vibration of the free carboxylate ion, respectively.²¹ These changes confirmed that KGM had reacted with chloroacetic acid.

The value of the $-\text{OH}$ stretching frequency has been used to give CMKGM as a measure of strength of hydrogen bonds.²² The intermolecular H-bonded $-\text{OH}$ stretching vibration for the CMPU80 sheet exhibited an absorption band at 3440 cm^{-1} , compared with that of CMKGM (3450 cm^{-1}) and $-\text{NH}$ band of WPU (3300 cm^{-1}). Moreover, the absorption peak of intermolecular H-bonded $-\text{OH}$ became broad, and the intensity increased as CMKGM content increased. These results suggested that the hydrogen bonds of CMKGM or WPU themselves were broken, and new, stronger hydrogen bonding between CMKGM and WPU formed. Meanwhile, the absorption peak at 3136 cm^{-1} for CMPU80, attributed to intramolecular "chela" H-bonded $-\text{OH}$, shifted to a wavenumber higher than that of pure CMKGM (3131 cm^{-1}), implying that intramolecular hydrogen bonds in CMKGM might be partly destroyed. However, all peaks for the CMPU30 sheet were almost simply overlapped by those of CMKGM and WPU, indicating poor miscibility between the two polymers.

The absorption peak at 1728 cm^{-1} for WPU was attributed to the stretching vibration of urethane carbonyl groups.^{23,24} With an increase of CMKGM content, the peak of urethane carbonyl groups in the blend sheets decreased and shifted to a lower wavenumber, implying that the stronger interactions between CMKGM and WPU occurred in the blend sheets.

The storage modulus (E') and loss factor ($\tan \delta$) of the sheets as functions of temperature are shown in Figures 2 and 3, respectively. The E' value of the blends increased dramatically with an increase of CMKGM content, indicating that CMKGM was of critical importance to enhance the strength and stiffness of the blends. The value of E' for WPU decreased sharply at -29°C , accompanying the glass transition (T_g) of the soft segments.²⁵ However, the CMKGM, CMPU80, and CMPU60 sheets remained at relatively high storage modulus even at temperatures up to 200°C . In particular, the CMPU80 sheet in the blends was characterized by E' behavior close to that of the CMKGM sheet in the range of temperature from -80 to 200°C , implying a reinforcement of CMKGM matrix with WPU particles.²⁶

As shown in Figure 3 and Table I, the original WPU exhibited a loss peak ($\tan \delta$) at -29°C corresponding to the soft-domain glass transition.²⁵ Meanwhile, the

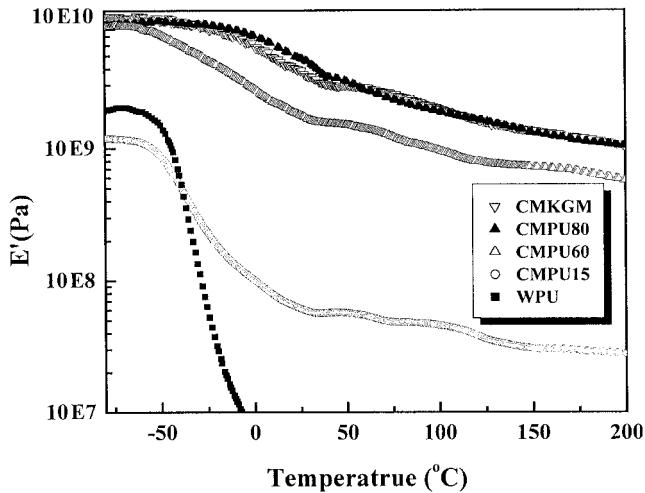


Figure 2 Storage modulus (E') as a function of temperature for the sheets.

T_g of pure CMKGM was observed at 110°C. When a small amount of CMKGM was added to WPU, the damping peaks of both WPU and CMKGM for the blends shifted outward, suggesting a certain degree of phase separation. With an increase of CMKGM content from 30 to 100 wt %, two damping peaks shifted

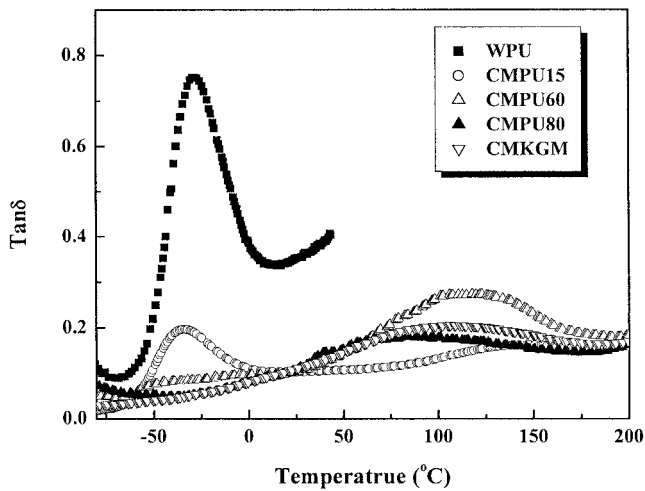


Figure 3 $\tan \delta$ as a function of temperature for the sheets.

TABLE I
Glass-Transition Temperature of Sheets Obtained from $\tan \delta$ Peak

CMKGM content (wt %)	T_g (°C)	
	WPU	CMKGM
0	-29	—
15	-33	147
60	-5	106
80	—	79
100	—	110

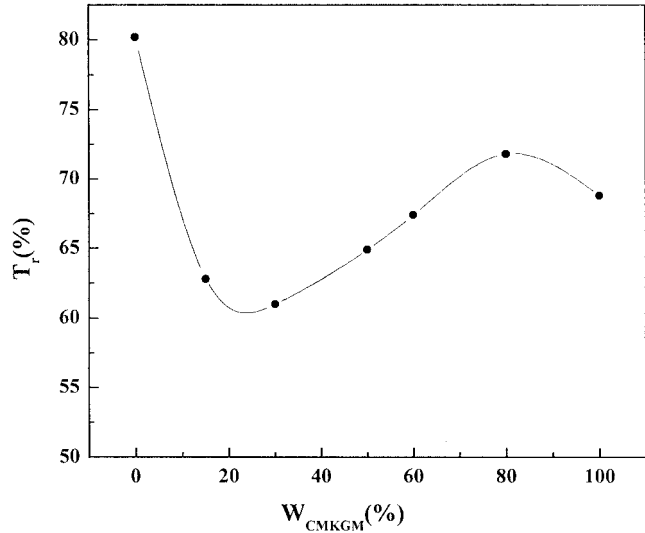


Figure 4 Dependency of optical transmittance (T_r) on CMKGM content at 800 nm of the sheets.

toward each other, implying a certain degree of miscibility. It is noted that the plateau region of WPU disappeared in the CMPU80 blend sheet, and a new transition region was observed at 79°C, which was basically identical with a theoretical value of T_g of the two blends. The theoretical value was given by the following expression²⁷:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (2)$$

where W_1 and W_2 are the weight fraction of WPU and CMKGM, respectively. The results indicated that the blend sheet with 80 wt % CMKGM exhibited good miscibility. The sharpness and height of the damping peaks give information about the degree of order and freedom of motion of molecules in the soft domains.^{25,28} From a plot of $\tan \delta$ versus temperature, the magnitude of the damping peaks of WPU in the blends decreased. An explanation for the WPU–CMKGM composite is that the soft segments of WPU penetrated into the rigid molecule of CMKGM, and the movements of the soft domains were restricted because of the hardness of the main chain for CMKGM, resulting in a much higher glass-transition temperature.

The transparency of the sheets is an auxiliary criterion by which to judge the miscibility of the composite materials.²⁹ Optical transmittances (T_r) at 800 nm of the sheets are shown in Figure 4. When the CMKGM content was not greater than 60 wt %, the T_r of the blend sheets was lower than that of either CMKGM or WPU, indicating a certain degree of phase separation. However, the blend sheets with CMKGM content greater than 60 wt % exhibited higher T_r than that of the pure CMKGM sheet. In particular, the light transmittance of CMPU80 achieved 71.8%, implying good

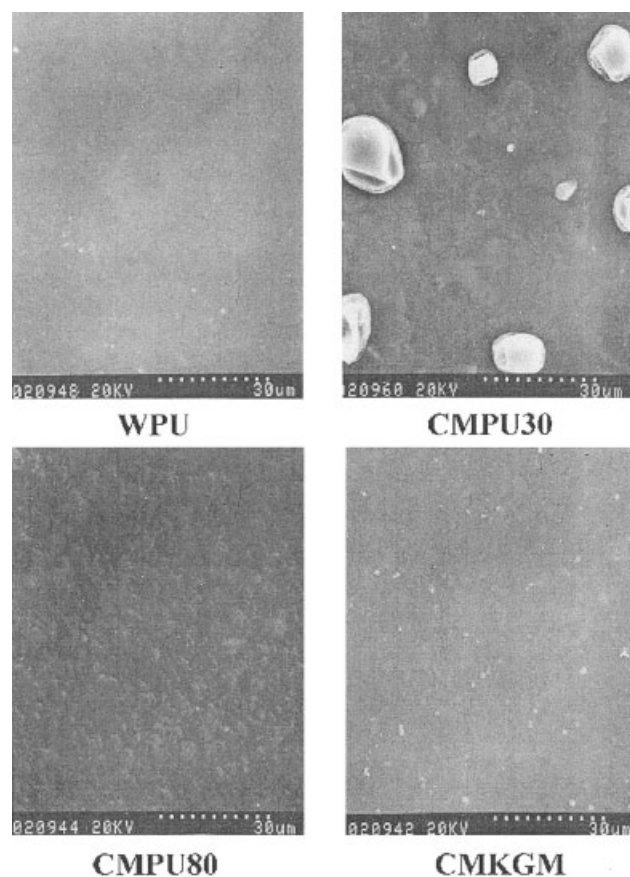


Figure 5 SEM images of the surfaces of the sheets.

miscibility and stronger intermolecular interaction between CMKGM and WPU.

Figure 5 shows the SEM micrographs of the free surfaces of the WPU, CMPU30, CMPU80, and CMKGM sheets, respectively. A homogeneous morphology for CMKGM and WPU was observed. It is possible to observe a nucleating structure resulting from aggregation of smaller nuclei for the CMPU30 sheet, suggesting a certain degree of phase separation. Nevertheless, the surface of the CMPU80 sheet exhibited a typical “sea-island” structure with vague interface and the average size of “islands” of about $2 \mu\text{m}$, indicating good miscibility between CMKGM and WPU. In this case, a small amount of WPU was dispersed in the continuous phase of CMKGM to produce strong adhesion force, resulting in formation of relatively dense architectural structure. In addition, SEM micrographs of the cross sections of sheets of WPU, CMKGM, and blends are shown in Figure 6. Homogeneous structures were observed for the inside of both WPU and CMKGM sheets. The cross section for CMPU30 exhibited a rough structure, suggesting partial phase separation. However, a dense architectural structure was observed for CMPU80, implying that intermolecular hydrogen bonding between the two polymers might reinforce the interfacial adhesion in the

blend sheet. In view of the SEM analysis, the CMPU80 sheet displayed better miscibility than that of CMPU30.

The WAXD patterns for the sheets are shown in Figure 7. WPU showed a broad crystalline peak around $2\theta = 20^\circ$.^{30–32} No characteristic crystalline peak for CMKGM was detected in the WAXD pattern, indicating an amorphous nature. With an increase of CMKGM content, the intensities of the diffraction peak corresponding to $2\theta = 20^\circ$ for the blend sheets gradually decreased, and the shape of the diffraction peak became increasingly broader, which suggested the presence of an interaction between CMKGM and WPU.

Properties of blend sheets

The dependency of the tensile strength (σ_b) and Young's modulus (E') on CMKGM content for the blend sheets is shown in Figure 8. With an increase of CMKGM content, both strength and modulus of the blend sheets increased significantly. This indicated that strong interaction between WPU and CMKGM occurred in the composites, resulting in great enhancement of σ_b and E' . Moreover, the CMPU80 sheet exhibited much higher tensile strength (89.1 MPa) than that of either CMKGM (56.4 MPa) or WPU (3.2 MPa).

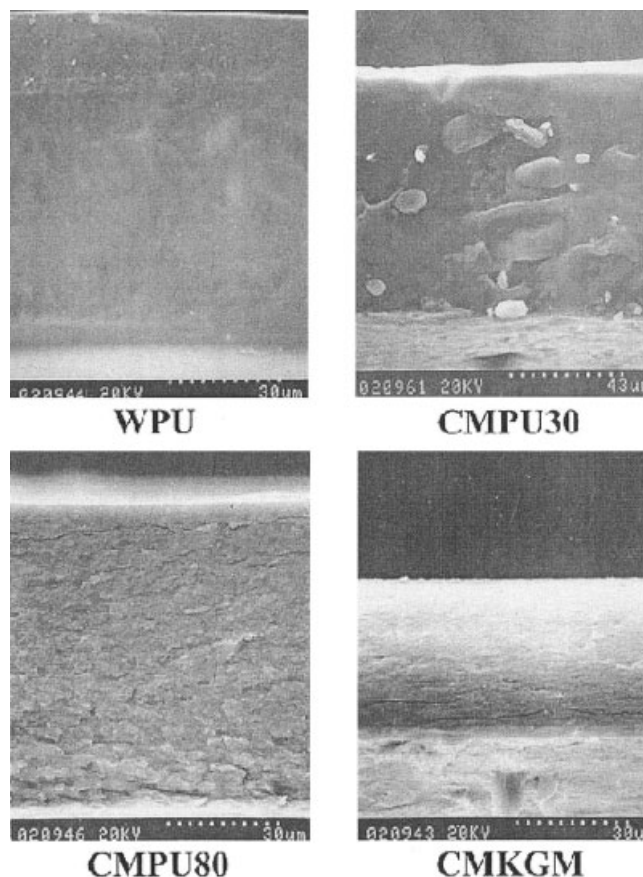


Figure 6 SEM images of the cross sections of the sheets.

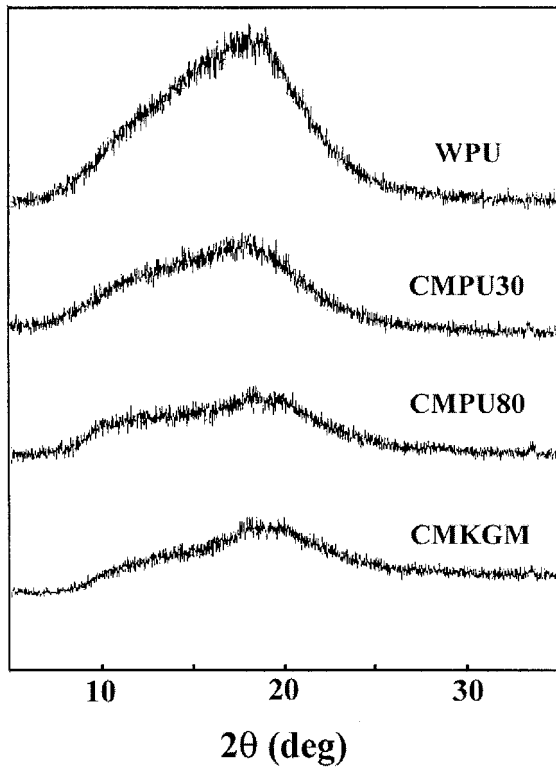


Figure 7 WAXD patterns of sheets of WPU, CMKGM, and blends.

The results supported the conclusion of good miscibility for the CMPU80 sheet obtained by DMA, UV, and SEM measurements. Figure 9 shows the dependency of elongation at break (ϵ_b) on CMKGM content for the blend sheets. The ϵ_b values of the blend sheets were lower than that of the WPU sheet. However, all the blend sheets displayed higher ϵ_b values than that

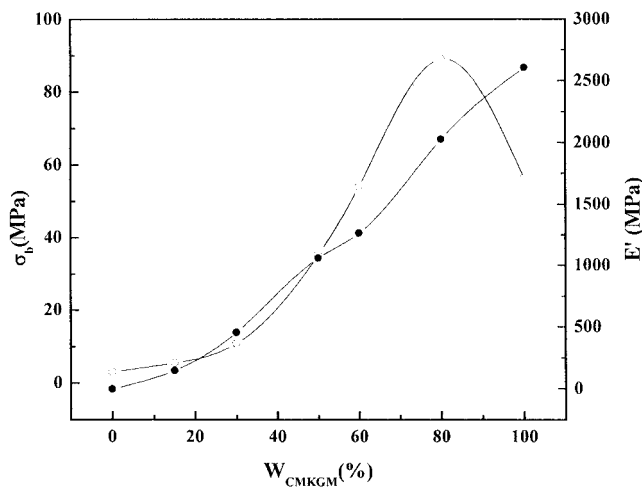


Figure 8 Dependency of tensile strength (σ_b , ○) and Young's modulus (E' , ●) on CMKGM content for the blend sheets.

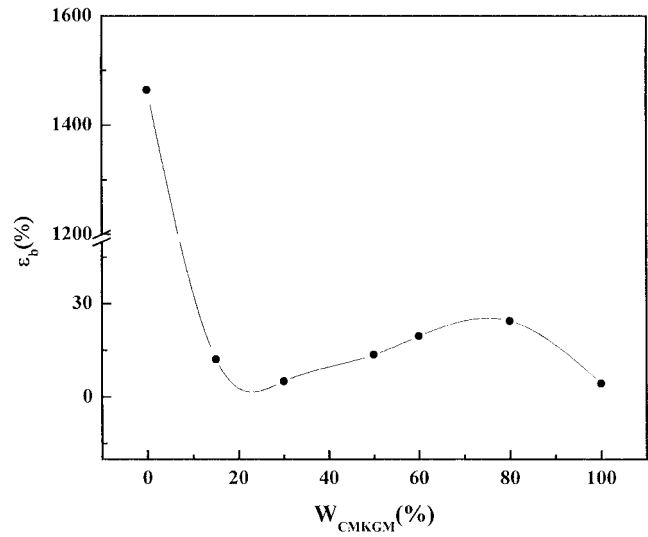


Figure 9 Dependency of elongation at break (ϵ_b) on CMKGM content for the blend sheets.

of pure CMKGM ($\epsilon_b = 4.3\%$), particularly CMPU80 ($\epsilon_b = 24.7\%$), which was attributed to the enhancement of flexibility caused by introducing WPU.

Thermal degradation patterns of the sheets are shown in Figure 10. The WPU sheet exhibited only one weight loss step in the course of thermal degradation. WPU could be stable up to 220°C, and then decomposed to give greatest weight loss in the range from

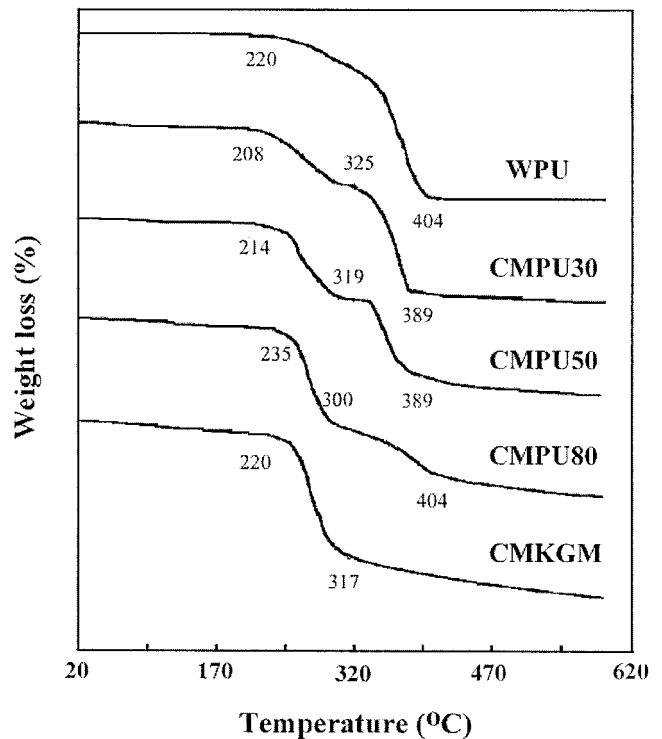


Figure 10 TGA thermograms of the sheets under nitrogen atmosphere.

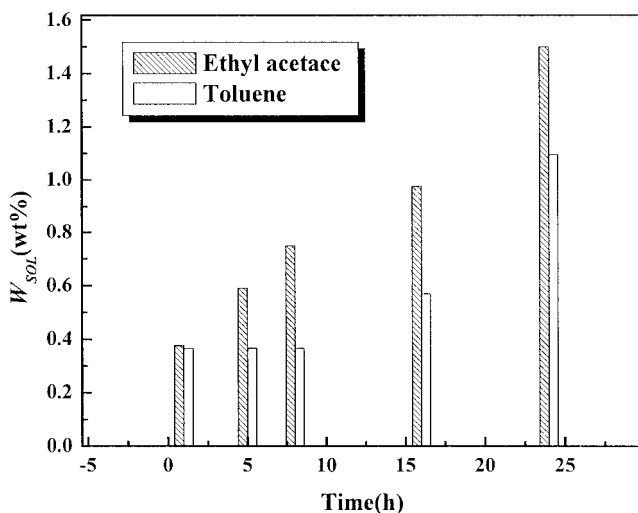


Figure 11 Dependency of the swelling degree (W_{sol} , wt %) on time for the CMPU80 sheet in ethyl acetate and in toluene.

320 to 404°C.³³ The CMKGM sheet showed two steps of active weight loss with elevation of temperature: a small weight loss at 20–220°C was attributed to the release of moisture and the breaking of intermolecular hydrogen bonds. From 220 to 317°C, the weight loss resulted from the breaking of intramolecular hydrogen bonds and unzipping of the molecular chains. In the blend sheets, a sharp decrease in weight loss in the temperature range of about 200–300°C was attributed to CMKGM decomposition; the weight loss at about 300–400°C was ascribed to WPU degradation. Interestingly, the onset temperature of CMKGM decomposition for the CMPU80 sheet (234°C) was higher than that of the pure CMKGM sheet (220°C), indicating relatively high thermal stability because of the reinforcement of intermolecular interaction between the two polymers. In addition, the residues of the blend sheets at 600°C increased from 11.2 to 24.9 wt % with an increase of CMKGM content from 30 to 80 wt %, suggesting an enhancement of thermal stability for the blend materials.

The dependency of the degree of swelling for the CMPU80 sheet in ethyl acetate or toluene on the swelling time is shown in Figure 11. Whether ethyl acetate or toluene was used as solvent, the degree of swelling remained at a low value with increasing time. Even if the CMPU80 sheet was immersed in ethyl acetate and toluene for 24 h, the values of W_{sol} were 1.1 and 1.5 wt %, respectively. In the blend system, the continuous phase should govern the swelling property, so it can be believed that CMKGM as continuous phase played an important role in enhancement of organic solvent resistance for the blend materials.

CONCLUSIONS

In an aqueous system, WPU and CMKGM were satisfactorily blended to obtain environmentally friendly ma-

terials with good mechanical and thermal properties. In terms of the experimental results, the blend materials possess good, or a certain extent of, miscibility over the whole ratio range of WPU to CMKGM. There is better miscibility between WPU and CMKGM in the blend sheet with 80 wt % CMKGM than that of other blends. Moreover, tensile strength, Young's modulus, and thermal stability of the blend sheets increased significantly with an increase of CMKGM content. In particular, the tensile strength of the CMPU80 sheet was higher than that of either CMKGM or WPU. The results indicated that strong interaction of hydrogen bonds between CMKGM and WPU occurred in the blends, and enhanced the interfacial adhesion of two polymers to impart relatively good mechanical and thermal properties.

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