

Miscibility and Properties of Blend Membranes of Waterborne Polyurethane and Carboxymethylchitin

Ming Zeng, Lina Zhang, Niangui Wang, Zhichao Zhu

Department of Chemistry, Wuhan University, Wuhan 430072, China

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ABSTRACT: We prepared a series of blend membranes by blending waterborne polyurethane (WPU) and carboxymethylchitin (CMCH) in aqueous systems. The effects of CMCH content on the miscibility, morphology, thermal stability, and mechanical properties of the blend membranes were investigated by dilute solution viscometry (DSV), Fourier transform infrared spectroscopy, wide-angle X-ray diffraction (WXR), scanning electron microscopy, dynamic mechanical analysis (DMA), thermogravimetric analysis, ultraviolet (UV) spectroscopy, and tensile testing. The miscibility parameter of the WPU/CMCH aqueous solution obtained by DSV predicted that the blends of WPU and CMCH were miscible or partially miscible. Moreover, the partial miscibility of the blend membranes over the entire compo-

sition range were confirmed by FTIR, WXR, DMA, and UV spectroscopy to support the conclusion from DSV. New hydrogen bonds were formed between CMCH and WPU in the blend membranes, resulting in strong intermolecular interactions. By inducing the CMCH, we improved the tensile strength, thermostability, and organic solvent resistance of the blend membranes significantly. Therefore, this study not only provided a novel way to prepare an environmentally friendly material but also expanded the application of chitin and CMCH. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1233–1241, 2003

Key words: polyurethanes; blends; membranes

INTRODUCTION

Recently, natural polymers and their derivatives as renewable and biodegradable materials have attracted considerable attention because of the serious pollution caused by synthetic materials and the shortage of resources.¹ Chitin, a (1→4)-linked polysaccharide composed of 2-acetamido-2-deoxy- β -D-glucopyranose residues, is widely distributed in nature as the skeletal material of crustaceans, insects, and mushrooms and as the cell walls of bacteria.² Materials made of chitin or modified chitin have the attractive advantages of being nontoxic, biodegradable, and antibacterial and having relatively good biocompatibility, which offer large unexplored commercial applications.^{3,4} However, one limitation of the use of chitin is that it is insoluble in aqueous solvents. Water-soluble derivatives of chitin formed by chemical modification have been the subject of extensive research in past decades. Carboxymethylchitin (CMCH) is water-soluble at neu-

tral pH values and has potential applications in industry, pharmacy, personal care, agriculture, and biotechnology.^{5,6}

As an effort to be more environmentally conscious, regulatory changes have been implemented to restrict solvent emissions, in particular volatile organic compounds.⁷ Polyurethane has great applicability in the reduction of organic solvents by converting the traditional system to the aqueous system.⁸ Waterborne polyurethane (WPU), as a nontoxic, nonflammable, and environmentally friendly material, has a broad range of applications, including plastics coating, automatic finishing, industrial finishing, and corrosion-protection coating.^{9–13} The complex materials composed from CMCH and WPU in aqueous solution are believed to improve the function and properties. Polymer blends continue to be a subject of intense investigation because of the simplicity and effectiveness of mixing two different polymers to produce new materials, from both academic and industrial views, in the last decades.¹⁴ Blends of polymers may result in a reduction in the basic cost and an improvement in processing and may also enhance the properties to be maximized.¹⁵ Therefore, blend membranes from WPU and CMCH in aqueous systems not only provide potential applications as versatile or functional materials but also protect the environment and conserve limited petroleum resources. Properties of polymer blends depend mainly on the state of miscibility, which is generally considered the result of specific interactions

Correspondence to: L. Zhang (lnzhang@public.wh.hb.cn).

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between polymer segments.¹⁶ They can be detected by differential scanning calorimetry, dynamic mechanical analysis (DMA), neutron scattering, inverse gas chromatography, electron microscopy, spectroscopy, and viscometry.^{17–20} In this work, WPU and CMCH were synthesized and then blended in aqueous systems to prepare new membranes. The compatibility of the blend membranes were measured by dilute solution viscometry (DSV). The effects of CMCH content on the morphology, miscibility, thermal stability, tensile strength (σ_b), and solvent resistance of the blend membranes were investigated by Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WXR), scanning electron microscopy (SEM), DMA, thermogravimetric analysis (TGA), ultraviolet (UV) spectroscopy, tensile testing, and solvent swelling testing.

EXPERIMENTAL

Synthesis of WPU

Anionic WPU was prepared through a two-stage polymerization process.^{21,22} Commercial 2,4-toluene diisocyanate (TDI; Shanghai Chemical Co., China) was vacuum-dried at 80°C for 2 h and was used as hard segments. Polypropylene glycol (PPG; weight-average molecular weight = 1000; Nanjing Chemical Factory, China) was vacuum-dried at 105°C for 5 h and was used as soft segments. Dimethylol propionic acid (DMPA; Chengdu Polyurethane Co., China) was also vacuum-dried at 110°C for 2 h and was used as a chain extender and an anionic center. Triethylamine (TEA; Shanghai Chemical Co., China) and ketone as a neutralized reagent and a solvent, respectively, were treated by 3-Å molecular sieves for more than a week to dehydrate them before use. The dry PPG was heated to 75°C with mechanical stirring in a three-necked flask; TDI was added in one portion, and stirring was continued at 75°C for 2.5 h. Then, an equivalent amount of dry DMPA was added in one portion to the stirred mixture. The reaction was carried out for 2–3 h until the NCO-group content reached a given value, as determined by dibutylamine back titration.²³ Then, ketone was added to reduce the viscosity of the prepolymer. Finally, the product was cooled to 60°C and was 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 17 wt %.

Preparation of CMCH

CMCH was prepared through a modified reaction process in which the NaOH amount used was lower than reported.^{24,25} Chitin was supplied by Zhejiang Yuhuan Sea Biochemical Co., China and its viscosity-

average molecular weight (M_n) and degree of acetylation were 1.31×10^6 and 92.5%, respectively. It was used without further purification. Chloroacetic acid and isopropyl alcohol were analytical grade.

Chitin (10 g) was mixed with 50 wt % aqueous NaOH (20 g) and stirred for 1 h, and then, the mixture was kept overnight at -18°C . The resulting mixture was dissolved in isopropyl alcohol (140 mL), chloroacetic acid (11 g) was added into the mixture, and the mixture was kept at room temperature for 2 h and at 60°C for 2 h. The solution was neutralized with HCl at 40°C, yielding a precipitate of CMCH. The CMCH was dissolved in water (240 mL) with stirring for 2 h. The brown and viscous solution was centrifuged at 4000 rpm for 15 min, and the supernatant was slowly added to 500 mL of acetone. The fibrous precipitate was washed with ethanol and 80 wt % aqueous ethanol. The product was vacuum-dried and stored in a desiccator. The M_n of the resulting product was determined by the viscometry method⁶ as 1.54×10^5 .

Preparation of the blend membranes

CMCH (1 g) was dissolved in 25 g of water to obtain a 4 wt % CMCH solution. The WPU was mixed with varying amounts of CMCH solution at room temperature for 1 h with stirring. Then, the mixture was cast on a glass plate mold and dried at room temperature for 7–10 days to obtain membranes. By changing the weight ratio of CMCH in the blend membranes (i.e., to 15, 35, 50, 65, 85, and 95 wt %), we prepared a series of blend membranes and coded them as CMPU15, CMPU35, CMPU50, CMPU65, CMPU85, and CMPU95, respectively. Membranes from pure CMCH and WPU were coded as CMCH and WPU, respectively.

Miscibility measurements by viscometry

An Ubbelohde capillary viscometer (Chinese Academy of Sciences, China) was employed to measure the reduced specific viscosities (η_{sp}) where η_{sp}/c is the specific viscosity and c is the polymer concentration and inherent viscosities ($\ln \eta_r/c$) of CMCH and its blend solutions in 0.1M NaCl aqueous solution and that of WPU in water, respectively, at $30.0 \pm 0.1^\circ\text{C}$. The kinetic energy was negligible. A series of blend solutions were prepared with varied weight ratios of CMCH/WPU (1:0, 0.15:0.85, 0.35:0.65, 0.50:0.50, 0.65:0.35, 0.85:0.15, 0.95:0.05, 0:1); these were coded as CMCH, CMPU15, CMPU35, CMPU50, CMPU65, CMPU85, CMPU95, and WPU, respectively. The stock solution of each binary and ternary systems were prepared by dissolution with water up to a polymer concentration of 3×10^{-3} g mL⁻¹.

For a common dilute solution of a nonelectrolyte polymer, the reduced viscosity follows the linear relationship given by the Huggins equation:^{26,27}

$$\eta_{\text{sp}} = [\eta]c + bc^2 \quad (1)$$

$$b = k[\eta]^2 \quad (2)$$

where $[\eta]$, b and k are the intrinsic viscosity, the viscometric parameter, and the Huggins constant, respectively. For a mixture (m) of polymers 2 and 3 in a common solvent, $[\eta]_m$ and b_m are

$$[\eta]_m = [\eta]_2w_2 + [\eta]_3w_3 \quad (3)$$

$$b_m = (b_{22}^{1/2}w_2 + b_{33}^{1/2}w_3)^2 \quad (4)$$

where w_i represents the weight fraction of polymer i ($i = 2, 3$) in a polymer mixture (m).

The expression for the polymer-polymer interaction parameter in the mixture (b_m) is

$$b_m = k_m[\eta]_m^2 \quad (5)$$

For polymers 2 and 3, the parameters b_{22} and b_{33} can be represented by

$$b_{22} = k_2[\eta]_2^2 \quad (6)$$

$$b_{33} = k_3[\eta]_3^2 \quad (7)$$

When the long hydrodynamic interaction of pairs of single molecules is considered, the miscibility criterion of the miscibility parameter (α) can be obtained by

$$k_m^{id} = (k_2^{1/2}w_2[\eta]_2 + k_3^{1/2}w_3[\eta]_3)^2 / (w_2[\eta]_2 + w_3[\eta]_3)^2 \quad (8)$$

$$\alpha = k_m^{\text{exp}} - k_m^{id} \quad (9)$$

Here the experimental and theoretical k_m values can be obtained from eq. (5) and (8), respectively and k_2 and k_3 can be easily determined from eqs. (6) and (7), respectively. Thus the α is based on the comparison between experimental and theoretical k_m values. When α is 0 or greater, the polymer blend is miscible; when α is less than 0, the blend is immiscible.²⁰

Characterization

IR spectra of the samples were recorded on a FTIR spectrometer (model 1600, PerkinElmer Co., USA). The test specimens were vacuum-dried and then prepared by the KBr-disk method. Attenuated total reflection IR spectroscopy of the WPU membrane was also performed on the same instrument. The sample was taken at random on the flat membrane, and data were collected over 16 scans with a resolution of 4 cm^{-1} at room temperature.

WXR patterns were recorded on an X-ray diffraction instrument (XRD-6000, Shimadzu, Japan) with Cu $K\alpha$ 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 10 to 40°.

SEM micrographs were taken with a SEM microscope (X-650, Hitachi, Japan). The membranes were frozen in liquid nitrogen, snapped immediately, and then vacuum-dried. The surfaces and cross-sections of the membranes were sputtered with gold and then observed and photographed.

DMA was carried out with a dynamic mechanical thermal analyzer (DMTA-V, Rheometric Scientific Co., USA) at 1 Hz and at a heating rate of 5°C min^{-1} in a temperature range of -80 to 250°C. Specimens with typical size of 10 × 10 mm (length × width) were used.

TGA of the specimens 1 mm wide and 1 mm long were carried out with a thermobalance (PRT-2, Beijing Optical Instruments Factory, China) under an air atmosphere from 25 to 600°C at a heating rate of 10°C min^{-1} .

Optical transmittances (T , values) of the membranes were measured with a UV-visible spectrophotometer (Shimadzu UV-160A, Japan) at a wavelength of 800 nm, and the thickness of the membranes was about 100 μm .

σ_b and elongation at break (ϵ_b) of the samples were measured on a versatile tester (CMT-6503, Shenzhen SANS Test Machine Co., Ltd., China) according to the ISO6239-1986 standard with a tensile rate of 5 mm min^{-1} . The samples were 70 mm in length, 10 mm in width, with 50 mm in distance between the two clamps.

Solvent swelling tests of the membranes were performed with different solvents. The dry membranes were weighed (w_0) and then immersed into the solvent to prepare swelling membranes for 5 min or 24 h. The resulting membranes were taken out, and the excess solvent on the membrane was wiped off with a paper cloth to weigh. The degree of swelling was calculated by the following equation:

$$\begin{aligned} \text{Degree of swelling (wt \%)} \\ = [(w_s - w_0)/w_0] \times 100\% \quad (10) \end{aligned}$$

where w_s represents the weight of the swollen membrane.

To study the solvent resistance, we immersed the membranes in different solvents, including water, ethanol, acetone, and toluene at 35°C for 24 h.

RESULTS AND DISCUSSION

Miscibility of blend solutions

The results obtained by the DSV measurements are summarized in Table I. $[\eta]_m^{\text{exp}}$ and b_m^{exp} were calculated

TABLE I
Experimental and Calculated Viscosity Data for the Ternary Mixtures at 30°C

Sample	$[\eta]_m^{\text{exp}} \times 10^{-2}$ (mL/g)	$b_m^{\text{exp}} \times 10^{-4}$ (mL/g) ²	k_m^{exp}	$[\eta]_{\text{cal}} \times 10^{-2}$ (mL/g)	$\Delta[\eta] \times 10^{-2}$ (mL/g)	α
WPU	0.1106	0.003	0.2453	—	—	—
CMPU15	1.931	2.162	0.5808	1.933	-0.0024	0.4154
CMPU35	4.310	5.387	0.2900	4.363	-0.0532	0.1270
CMPU50	6.256	7.617	0.1946	6.185	0.0703	0.0322
CMPU65	8.187	13.68	0.2041	8.008	0.1795	0.0420
CMPU85	10.58	19.07	0.1703	10.44	0.1435	0.0084
CMPU95	11.75	25.97	0.1879	11.65	0.1031	0.0261
CMCH	12.26	24.31	0.1617	—	—	—

from the intercept and slope, respectively, of eq. (1). k_m^{exp} , $[\eta]_{\text{cal}}$, and α were calculated from eqs. (5), (3), and (9), respectively. $[\eta]_m^{\text{exp}}$ and $[\eta]_{\text{cal}}$ were experimental and theoretical $[\eta]$ values, respectively. $\Delta[\eta]$ was based on a comparison between experimental and theoretical $[\eta]$ values, i.e. $[\eta]_m^{\text{exp}} - [\eta]_{\text{cal}}$. Obviously, the measured $[\eta]$ values agreed with the prediction of $[\eta]_{\text{cal}}$ from eq. (3) within about 5%. Theoretically, the quantity b reflects the binary interactions between polymer segments.¹⁹ The b value of WPU was small, and that of CMCH was large. The b values of the blend solution increased with increasing CMCH. Furthermore, the b value of CMPU95 was even more than that of pure CMCH, indicating there existed specific interactions between the polymer pairs. The positive values of α indicated the blends of CMCH and WPU were miscible or partially miscible in the range of the entire composition ratio. Figure 1 shows α as a function of the weight fraction of CMCH. The α values decreased sharply with increasing CMCH from 35 to 50 wt %, and those of CMPU50, CMPU65, CMPU85, and CMPU95 hardly changed, with all at slightly more than zero, due to a certain degree of phase separation for the blend solutions with large amounts of CMCH. When the CMCH weight fraction was lower than 50

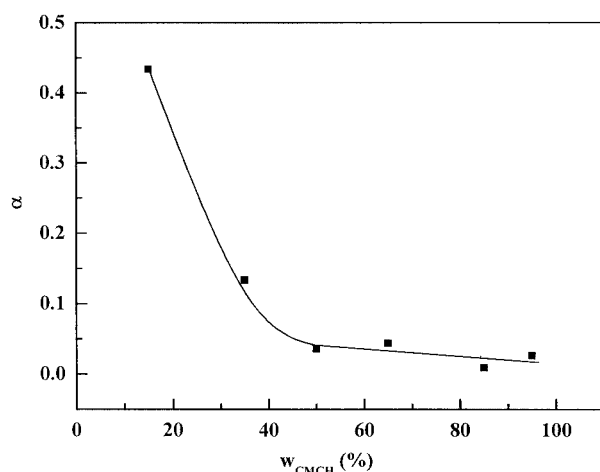


Figure 1 Dependence of α on CMCH content (w_{CMCH}) for the blend solutions at 30°C.

wt %, the α values predicted that the blend between CMCH and WPU was miscible.

Miscibility and morphology of the blend membranes

Figure 2 shows the FTIR spectra of chitin and CMCH. The absorptions at 1652 cm^{-1} (amide I band) and 1558 cm^{-1} (amide II band) hardly changed, but the C=O stretching band at 1735 cm^{-1} showed an apparent increase for CMCH, as compared with the spectrum of chitin. No significant *N*-deacetylation occurred during the reaction of carboxymethylation, and so, water-soluble CMCH was synthesized.^{6,28}

Figure 3(A) shows the IR spectra of the NH stretching region of the WPU and blend membranes. The NH stretching vibration exhibited a strong absorption peak at 3425 cm^{-1} arising from the hydrogen bonding between the NH and carbonyl groups for blend membranes, as compared with that of WPU (3300 cm^{-1}) and the —OH band at 3444 cm^{-1} for CMCH.²⁹ The

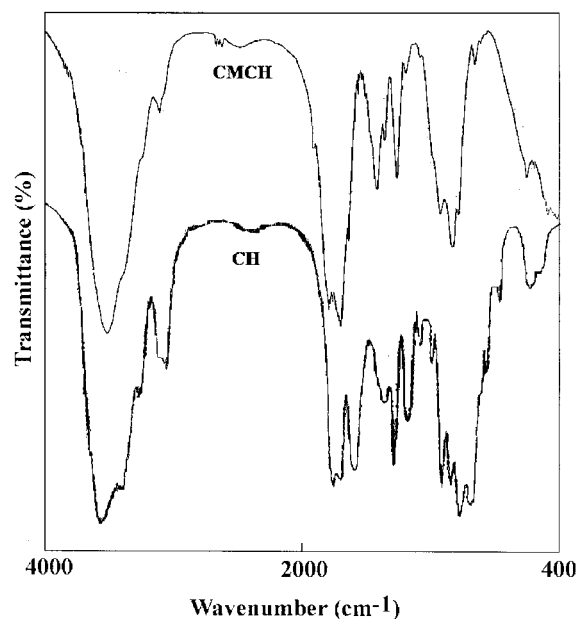


Figure 2 FTIR spectra of CMCH and chitin (CH).

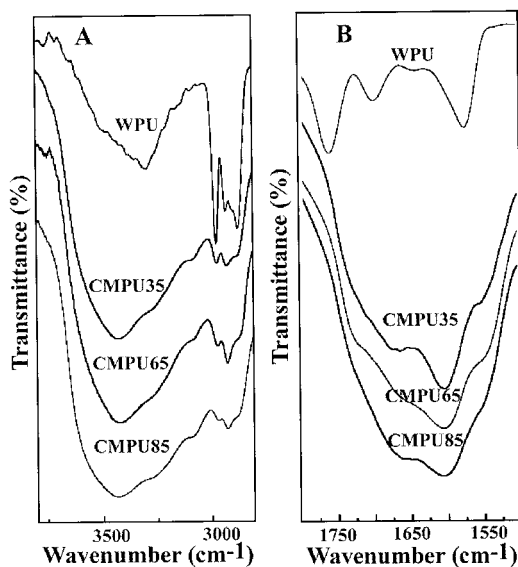


Figure 3 IR spectra of the membranes in the wavelength region (A) 3800–2800 and (B) 1800–1500 cm^{-1} .

intensity of hydrogen-bonded —NH increased as the CMCH content increased, suggesting that the hydrogen bonds of CMCH or WPU themselves were broken and new hydrogen bonds between CMCH and WPU were formed. An obvious shoulder peak appeared at 3250–3275 cm^{-1} , corresponding to the $\text{NH}\cdots\text{O}$ hydrogen bonding between the carboxyl groups of CMCH and the amide groups of WPU.³⁰ Moreover, the hydrogen-bonded NH stretching absorption around 3425 cm^{-1} for the blend membranes shifted to higher wavenumbers with increasing CMCH content, indicating an enhancement of free NH groups in the CMCH-rich blend membranes, which led to a reduction in interactions between CMCH and WPU in the CMPU65 and CMPU85 membranes.

The IR spectra of the carbonyl stretching region for WPU and the blend membranes are shown in Figure 3(B). The band at 1725 cm^{-1} in the WPU spectrum was attributed to the stretching of urethane carbonyl groups,^{30,31} whereas the band centered at 1657 cm^{-1} was assigned to the stretching of the hydrogen-bonded carboxylic carbonyl group from the DMPA unit.³² The band for the blend membranes centered around 1668 cm^{-1} resulted from the hydrogen-bonded carboxylic carbonyl from CMCH. With increasing CMCH content, the peak of urethane carbonyl groups for WPU (1725 cm^{-1}) in the blend membranes decreased, and the band around 1668 cm^{-1} for the hydrogen-bonded carbonyl of CMCH increased and shifted to a higher wavenumber. This implies that stronger interchain interactions between CMCH and WPU occurred in the blend membranes than in the original WPU.

The X-ray diffraction patterns for the membranes are shown in Figure 4. A broad diffraction peak for the

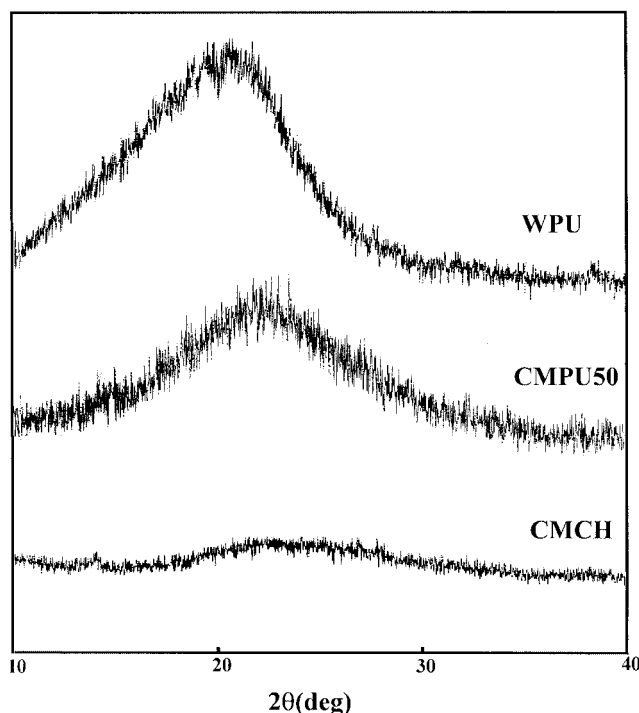


Figure 4 WXR D diffraction patterns of the membranes.

WPU membrane indicated an amorphous nature.³² No evidence of crystallization was found in the WXR D pattern for CMCH, suggesting a disruption of the crystalline structure by chemical modification.⁶ If

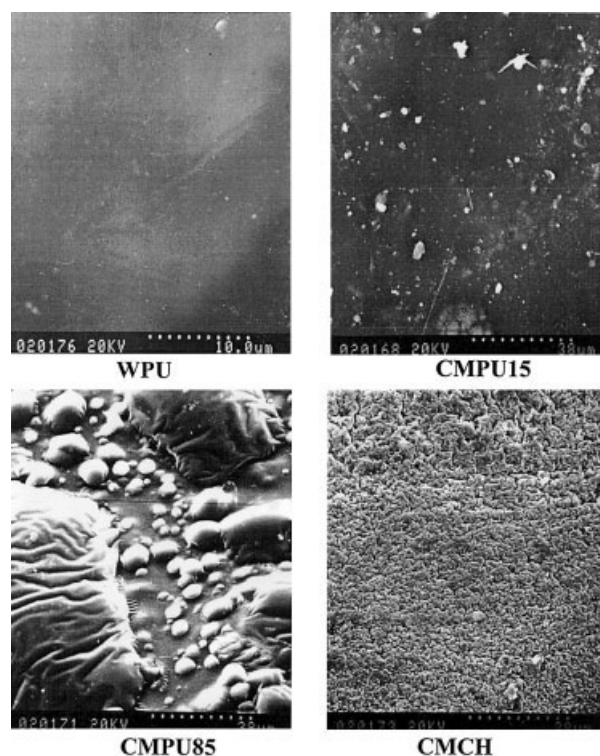


Figure 5 SEM micrographs of the surfaces of the membranes.

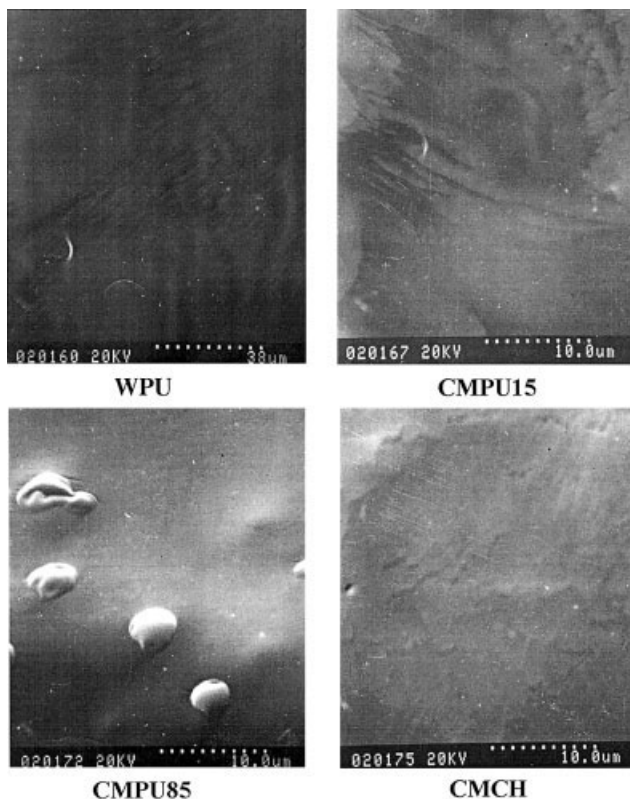


Figure 6 SEM micrographs of the cross-sections of the membranes.

WPU and CMCH were immiscible, each polymer would have had its own crystal region in the blend membranes, so the X-ray diffraction patterns would have been expressed as simply mixed patterns of the pure components. However, the broad scattering halo was around $2\theta = 22^\circ$ for CMPU50, as compared with that of WPU ($2\theta = 20^\circ$) and CMCH ($2\theta = 25^\circ$). In addition, the diffraction peak for the CMPU50 membrane was much lower than that of the pure WPU membrane. These results suggest that intermolecular

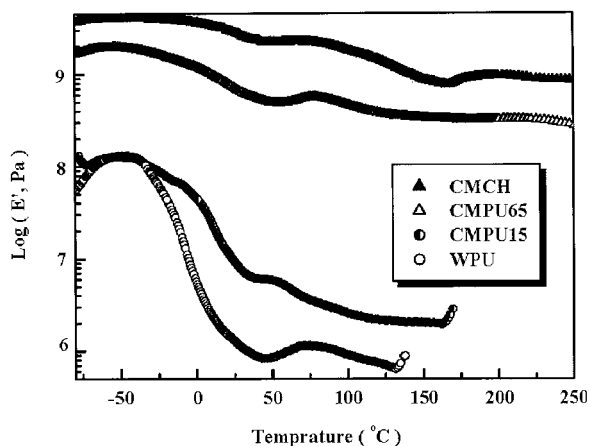


Figure 7 Log E' as a function of temperature for the membranes.

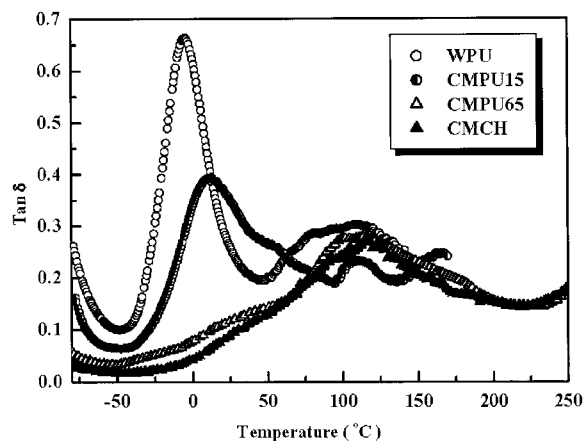


Figure 8 Tan δ as a function of temperature for the membranes.

hydrogen bonding interactions between WPU and CMCH must have been present in the blends, which destroyed the original molecular orientation of WPU and resulted in some changes in the WXR D patterns of the blends.^{33,34}

Figure 5 shows the SEM photographs of the free surfaces for the WPU, CMCH, and blend membranes. A homogeneous morphology was displayed for WPU membranes, whereas packed particles were observed for CMCH. The surfaces of the blend membranes exhibited “sea island” structures, namely, an island of CMCH particles dispersed in the sea of the WPU matrix. The presence of round particles immersed in a homogeneous matrix was observed for the CMPU15 membrane. For the CMPU85 membrane, we observed a nucleating structure with a large variation in size. There may have been smaller nuclei of one or both components included in the round structure. The SEM photographs of the cross-sections of the WPU, CMCH, and blend membranes are shown in Figure 6. Homo-

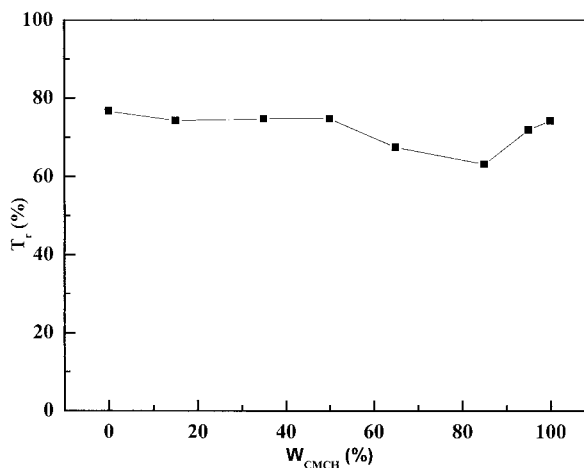


Figure 9 CMCH content (W_{CMCH}) dependence on T_r of the membranes at 800 nm.

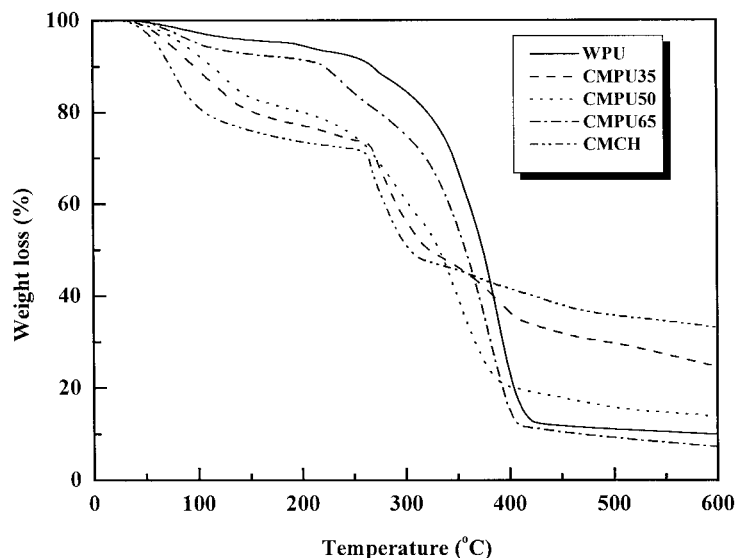


Figure 10 TGA thermograms of the membranes under an air atmosphere.

geneous structures in the inner region were observed for WPU, CMPU15, and CMCH membranes. In view of the SEM analysis, the CMPU15 membrane showed a better miscibility between CMCH and WPU than CMPU85. This suggests that hydrogen bonding between CMCH and WPU may have enhanced the interfacial adhesion in the blend membranes.³⁵

The storage modulus (E') and $\tan \delta$ of the membranes as functions of temperature are shown in Figures 7 and 8. E' values of WPU and CMPU15 membranes decreased dramatically with increasing temperature. However, the CMCH and CMPU65 membranes had high E' values even when the temperature was above 200°C, and the E' values for the blend membranes significantly increased with increasing CMCH content from 15 to 65 wt %, indicating that the CMCH played a role in the enhancement of the strength and stiffness.

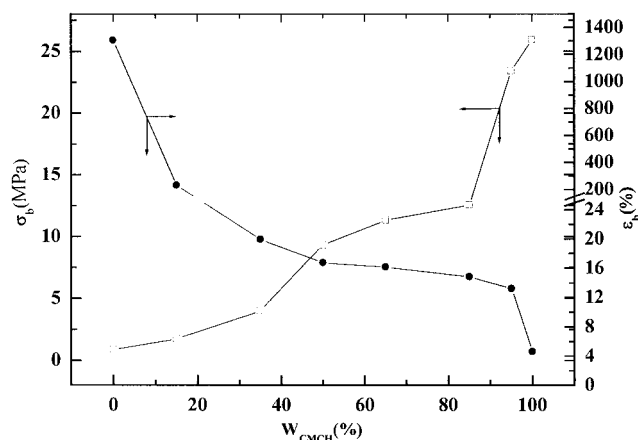


Figure 11 CMCH content (w_{CMCH}) dependence of the σ_b (\square) and ϵ_b (\bullet) of the membranes.

Usually, the α -relaxation peak reflects the glass-transition temperature and may be analyzed to provide information about the motion of molecules. If the two starting materials have phase separation and prevent interaction, two glass-transition peaks would be expected.^{36,37} The damping peaks of both WPU and CMCH for the blend membrane shifted toward each other, indicating that the CMPU15 and CMPU65 membranes were miscible to a certain degree. These findings support the conclusions obtained by SEM, DSV, WXR, and IR analysis.

The transparency of the membranes is an auxiliary criterion used to judge the miscibility of composite materials.³⁸ T_r values of the membranes at 800 nm are shown in Figure 9. The blend membranes with a CMCH content lower than 50 wt % exhibited a slightly higher T_r than the pure CMCH membrane, suggesting a certain degree of miscibility and a strong interaction between CMCH and WPU. However, with increasing CMCH content, the T_r of the blend membranes decreased and was lower than both CMCH and WPU as CMCH content increased from 65 to 95%, indicating a certain degree of phase separation.

Properties of the blend membranes

The thermal degradation patterns of the membranes are shown in Figure 10. The small weight loss at 20–150°C was assigned to the release of moisture and TEA from the samples. The weight losses at 400–600°C were believed to be caused by oxidation and degradation. The CMCH membrane exhibited two steps of active weight loss with elevating temperature, but the WPU membrane exhibited only one weight loss at 335–420°C in the course of thermal degradation. The greatest weight loss, in the range from 330 to

TABLE II
Degree of Solvent Swelling (wt %) for the Membranes

Sample	Methanol ^a	Ethanol ^a	Toluene ^a	Acetone ^a	Isopropyl alcohol ^a	Water ^a	Acetone ^b	Water ^b
WPU	29.17	29.67	17.12	26.99	23.91	0.44	38.68	16.34
CMPU15	24.31	24.48	14.17	26.47	17.73	13.64	29.70	354.1
CMPU35	16.92	21.50	13.87	23.25	17.24	37.71	27.42	Soluble
CMPU50	10.70	15.66	4.41	21.00	10.22	88.42	24.31	Soluble
CMPU65	5.99	13.81	3.85	17.33	9.73	214.6	21.22	Soluble
CMPU85	2.17	13.60	3.34	17.01	7.14	300.6	19.99	Soluble
CMPU95	1.87	12.81	2.15	16.75	6.70	336.5	19.76	Soluble
CMCH	0.49	11.45	0.26	13.37	5.86	362.8	14.54	Soluble

^a 5 min.

^b 24 h.

370°C, for the WPU and blend membranes was attributed to the onset of WPU decomposition.³⁹ A sharp drop in weight loss at 268 and 292°C for the CMPU50 and CMPU65 blend membranes, respectively, were ascribed to the decomposition of CMCH. Interestingly, the residues at 600°C of the CMPU50 and CMPU65 membranes (20 and 25 wt %) were higher than that of the WPU membrane (11 wt %), suggesting an enhancement in the thermal stability of the blend membranes due to intermolecular hydrogen bonding interaction.

The dependence of CMCH content for the blend membranes on σ_b and ε_b is shown in Figure 11. The values of σ_b for the blend membranes increased from 1.76 to 23.41 MPa with an increase in CMCH content from 15 to 95 wt %; meanwhile, ε_b decreased from 232 to 13.24%. The blend membranes showed a higher σ_b than the pure WPU membrane (0.89 MPa) and a higher ε_b than the pure CMCH membrane (4.64%). Therefore, the CMCH in the blend membranes strengthened the materials.

The solvent swelling test is a good method to determine the solvent resistance of blend membranes. The membranes in various solvents were swollen for 5 min and 24 h, and the results are summarized in Table II. The content of WPU as the continuous phase in the blend membranes, confirmed by the results from SEM, should have governed the properties of solvent resistance for the blends. It is well known that most WPUs are linear thermoplastic polymers with very little gel content, which allows solubility in solvents. On the basis of the data, the organic solvent resistance of the blend membranes increased with increasing CMCH

content. Therefore, the CMCH played an important role in the enhancement of the organic solvent resistance for the blend membranes.

The solubility of the membranes in different solvents is listed in Table III. None of the membranes could be dissolved in organic solvents. The CMCH-rich membrane was soluble in water. However, the CMPU15 membrane was insoluble in water, indicating that the solvent resistance of the blend membranes was enhanced by the interactions between CMCH and WPU.

CONCLUSIONS

WPU and CMCH in aqueous systems were successfully blended to prepare environmentally friendly blend membranes. On the basis of DSV measurements, the values of α of CMCH/WPU in aqueous solution were positive or close to zero in any event, predicting that the blends were miscible or partially miscible. The partial miscibility of the blend membranes over the entire composition range were confirmed by IR, WXR, DMA, and UV spectroscopy. The thermal stability and σ_b of the blend membranes increased significantly, compared with the pure CMCH and WPU membranes. These results indicated the formation of new hydrogen bonds between WPU and CMCH in the blends. The strong interaction of hydrogen bonds between CMCH and WPU enhanced the interfacial adhesion in the blend membranes to give relatively good T_g values, thermostability, σ_{br} , solvent resistance and so on.

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TABLE III
Solubility of the Membranes

Sample	Water	Ethanol	Acetone	Toluene
WPU	×	×	×	×
CMPU15	×	×	×	×
CMPU95	○	×	×	×
CMCH	○	×	×	×

× = insoluble; ○ = soluble.

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