

Waterborne Polyurethane/Poly(vinyl alcohol) Membranes: Preparation, Characterization, and Potential Application for Pervaporation

Lulu Yao,¹ Cuiming Wu,¹ Zhengjin Yang,² Wenqiong Qiu,¹ Peng Cui,¹ Tongwen Xu³

¹School of Chemical Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China

²Department of Chemical Engineering, Tsinghua University, Beijing, People's Republic of China

³Laboratory of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, People's Republic of China

Received 16 January 2011; accepted 9 October 2011

DOI 10.1002/app.36377

Published online 15 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Waterborne polyurethane (PU) was prepared by the prepolymer mixing method with (3-aminopropyl)triethoxysilane in different dosages as the modifier. Then, it was mixed with poly(vinyl alcohol) (PVA) to get waterborne PU/PVA blending membranes. The membranes showed phase separation with the aggregations of the waterborne PU particles in a continuous phase of PVA. The possible cause for the formation of such a membrane morphology is explained. The physicochemical properties of the membranes were characterized. As the PVA content increased, the membrane's

swelling in water and the thermal stability decreased somehow, whereas the resistance to ethanol and the tensile strength were significantly improved. Membranes with higher alcohol resistance were chosen for the pervaporation separation of 80 wt % ethanol in water. The separation factor at 40°C reached 38.4, and the permeation flux was 128.0 g m⁻² h⁻¹. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E216–E224, 2012

Key words: polymer blends; polyurethanes; silicas; thermogravimetric analysis (TGA)

INTRODUCTION

In recent years, a significant emphasis has been placed on the use of waterborne coating systems because of their environmental friendliness. Among these, waterborne polyurethane (PU) has attracted extensive attention because of its excellent elasticity,

wear resistance, easy processing, and high flexibility.^{1–3} Hence, it has been tailored to various applications, including coating, printing, ink, adhesives, and fiber processing. The disadvantages of waterborne PUs are the poor dispersion stability in solution, lower mechanical properties, and water/solvent resistance.² To improve the performance of waterborne PUs, different methods have been employed, such as changing the soft and hard segments,^{3–5} blending with inorganic components,^{6–8} and grafting of silanes or hydrophobic monomers.^{9,10} Among these modification methods, blending is simple and can be easily applied. Nevertheless, most of the synthesized polymers cannot be dissolved well in water, and hence, the direct blending of waterborne PU with organic polymers is difficult. To overcome this problem, polymers such as polydimethylsiloxane can be incorporated into waterborne PU chains as the soft segment,¹ which makes the preparation process more complex.

Poly(vinyl alcohol) (PVA) is easily obtained and can be dissolved well in water. The merits of PVA are its high flexibility, good membrane-forming ability, low toxicity, and excellent solvent resistance.¹¹ Another advantage of PVA is that it can be easily crosslinked with aldehyde,¹² silanes,¹³ and other linkers. After suitable modification and crosslinking, its mechanical and thermal stability can meet the

Correspondence to: C. Wu (cmwu@ustc.edu.cn) or P. Cui (cuipeng@hfut.edu.cn)..

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 51003100 and 20736003.

Contract grant sponsor: Project for Development of Scientific Research of Hefei University of Technology; contract grant number: 2009HGXJ0059.

Contract grant sponsor: Provincial Natural Science Foundation of Anhui; contract grant number: 11040606M37.

Contract grant sponsor: Provincial Programs for Young Excellence of Universities; contract grant number: 2011SQRL008.

Contract grant sponsor: Open Project of Engineering Research Center of Biomass Materials, Ministry of Education; contract grant number: 10zxbk08.

Contract grant sponsor: National Basic Research Program of China (973 Program); contract grant number: 2009CB623403 and 2009CB623404.

Journal of Applied Polymer Science, Vol. 124, E216–E224 (2012)
© 2012 Wiley Periodicals, Inc.

requirements of different application fields, including pervaporation,^{14,15} diffusion dialysis,^{11,16} and fuel cells.^{17,18}

The purpose of this study was to explore the possibility of blending waterborne PU with PVA. Actually, the use of PVA as a porogen for PU to get highly water-vapor-permeable coatings has been applied in synthetic leather industries.¹⁹ Nevertheless, separation membranes from the blending of waterborne PU and PVA have rarely been reported. The membranes should possess high flexibility and good permeability to water and were tried in the pervaporation separation of water/alcohol mixtures. According to previous research,²⁰ pervaporation results are dominated to a high extent by the nature of different chains of the polymer. The use of waterborne PU may induce interesting pervaporation results because of the difference in hard and soft segments.

The homogeneity of the blending system was another focus of our study. To improve the homogeneity, silane was tried as a crosslinker and modifier. The functional groups of the silane could be linked with the waterborne PU chains, whereas the alkoxy-silane [$-\text{Si}(\text{OR})_3$] groups could undergo hydrolysis and condensation reactions with the $-\text{OH}$ groups of PVA.²¹ Hydrogen bonding between the silanol groups ($-\text{SiOH}$) and the $-\text{OH}$ groups of PVA could also improve the compatibility of the blending system.

As reported by Sardon et al.,¹⁰ waterborne PU emulsions crosslinked by a low dosage of (3-aminopropyl)triethoxysilane (APTES; <9.7 wt %) showed a narrow particle size distribution with no obvious aggregation of the Si-containing groups. Therefore, APTES was applied as a crosslinker for PU in this work. The properties of the obtained membranes were explored, including the swelling in water and ethanol, thermal stability, and mechanical strength.

EXPERIMENTAL

Materials

Isophorone diisocyanate, poly(propylene glycol) (PPG; molecular weight = 2000 g/mol), and dimethylol propionic acid (DMPA) were all industrial grade and were purchased from Hefei Anke Chemical Co. (Anhui, China). PVA was purchased from Shanghai Yuanli Chemical Co. (Shanghai, China), and its average degree of polymerization was 1750 ± 50 . The other reagents were analytical grade and were purchased from Shanghai Guoyao Chemical Co. (Shanghai, China). PPG was dried at 105°C *in vacuo* for 1 day before use, and the other chemicals were used as received. Deionized water was used.

Preparation of the waterborne PU emulsion

The waterborne PU emulsion was synthesized by the prepolymer mixing method with four main steps:

1. Step 1: Synthesis of the PU prepolymer: Into a three-necked bottle, PPG (11.70 g), trimethylolpropane (TMP; 0.17 g), DMPA (1.10 g), 1,4-butanediol (BD; 0.6 g), isophorone diisocyanate (7.4 g), butanone (5.0 mL), and dibutyltin dilaurate (0.05 mL) were added in sequence and stirred at 40°C for 1 h and at 80°C for 5 h. DMPA acted as the internal emulsifier, dibutyltin dilaurate acted as the catalyst, and BD acted as the chain extender. The molar ratio of $-\text{NCO}$ groups to the total amount of $-\text{OH}$ groups (from TMP, DMPA, PPG, and BD) was set as 1.5 : 1.
2. Step 2: Functionalization of the prepolymer with APTES: The solution from step 1 was cooled to 40°C . Then, APTES was added and mixed for 5–10 min to form a homogeneous solution.
3. Step 3: Quaternization with triethylamine (TEA): TEA was added dropwise into the solution and then mixed for 30 min. The molar ratio of TEA to DMPA was 1 : 1.
4. Step 4: Emulsification and chain expansion with ethylenediamine (EDA): The obtained quaternized precursor from step 3 was cooled to $25\text{--}28^\circ\text{C}$ and dispersed into distilled water at $5\text{--}15^\circ\text{C}$. Thereafter, an aqueous solution of EDA was added and stirred for 1 h to expand the polymer chains; this resulted in a light blue emulsion with a solid content of around 10%.

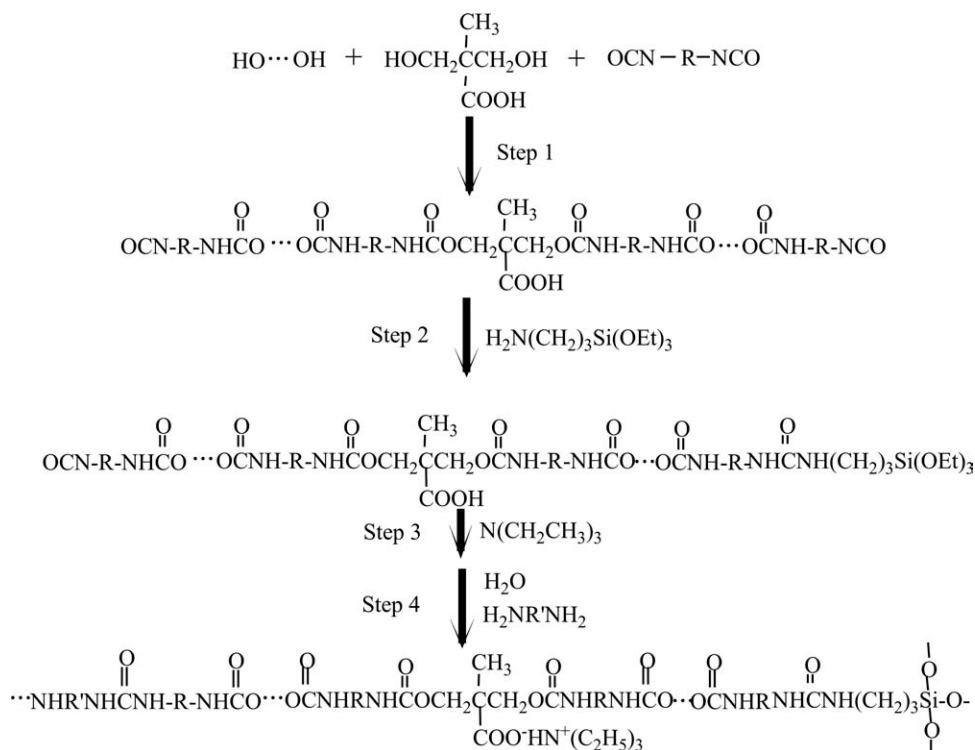
During step 2 of this procedure, the dosage of APTES (weight percentage in total waterborne PU) was varied from 1.78 to 3.36 to 4.97%. The waterborne PU emulsion with 1.78% APTES remained stable and transparent at room temperature for several days. Meanwhile, some deposition could be found in the emulsions from 3.36 and 4.97% APTES after around 16 h of preservation. Hence, all of the emulsions were used within 2 h after their preparation.

The reaction steps as described previously are illustrated in Scheme 1.

Preparation of the waterborne PU/PVA membrane

Prewedged PVA was immersed in water at room temperature for 1 day, then heated to 90°C at the rate of $10^\circ\text{C}/\text{h}$, and kept at 90°C overnight. The homogeneous and transparent solution (5 wt %) was cooled to room temperature before use.

The waterborne PU emulsion was then mixed with the PVA aqueous solution and stirred at 40°C



Scheme 1 Reaction procedures for the preparation of the waterborne PU emulsion.

for 2 days to obtain a waterborne PU/PVA emulsion. Then, the emulsion was cast onto a glass plate and dried in air. Afterward, it was heated from 50 to 120°C at a rate of 10°C/h and maintained at 120°C for 2.5 h to form the membranes.

During the previous preparation process, the dosage of PVA (weight percentage in waterborne PU + PVA mixture) was varied and a total of 12 membranes were obtained, as illustrated in Table I. The thickness of the membranes was in the range 0.05–0.07 mm.

Characterizations

Samples for Fourier transform infrared (FTIR) spectroscopy analysis were prepared in the form of KBr pellets and dried under an infrared lamp for 3–5 min. One FTIR spectrometer (Vector 22, Bruker, Switzerland) with a resolution of 2 cm⁻¹ and a spectral range of 4000–400 cm⁻¹ were used to record the spectra.

Wide-angle X-ray diffraction (WXR) measurements were conducted at room temperature with a Philips X'PERT PRO X-ray diffractometer (Japan). The membrane samples were scanned in the reflection mode at an angle of 2θ in a range from 1.5 to 30° at a speed of 8°/min.

The swelling of the membranes in water was measured as following: The dried membrane samples were weighed and immersed in distilled water at 40°C for 2 days. The surfaces of the wet membranes were then carefully dried with tissue paper,

and the membranes were weighed. The water uptake (W_R) was calculated as the relative weight gain per gram of the dry membrane sample. The swelling in ethanol was evaluated in similar way. The obtained ethanol uptake value was defined as Et_R .

The tensile properties were measured with an Instron universal tester (model 1185, Instron, USA) at 25°C with dumbbell-shaped specimens. The crosshead speed during elongation was 25 mm/min, whereas the initial gauge length was set as 20 mm. The tensile strength (TS) and elongation at break (E_b) values were recorded according to the average values of three measurements.

The morphologies of the hybrid membranes were observed with scanning electron microscopy (SEM; XT30 ESEM-TMP Philips). Before observation, the membrane samples were freshly fractured in liquid nitrogen and then coated with gold.

Thermogravimetry analysis (TGA) was conducted on a Shimadzu TGA-50H analyzer (Japan) under air flow at a heating rate of 10°C/min.

The effective area of the membrane for pervaporation was 2.167 × 10⁻³ m². The feed (80 wt % ethanol in water) was continuously circulated from a feed tank to the upstream side of the membrane at 40°C by a pump with an adjustable function of flow rate. The vacuum on the permeate side was maintained below 100 Pa. Two cold traps were applied to collect the permeate without rupture of the vacuum. The flux (J) was determined by measurement of the weight of permeate collected in the cold trap through the following equation:

TABLE I
Dosages of APTES and PVA for the Preparation of the Different Membranes

APTES (wt %) in waterborne PU	PVA (wt %) in the PVA + waterborne PU mixture	Membrane
1.78	0	M1
	33.3	M2
	50.0	M3
	66.7	M4
3.36	0	M5
	33.3	M6
	50.0	M7
	66.7	M8
4.97	0	M9
	33.3	M10
	50.0	M11
	66.7	M12

$$J = \frac{m}{At} \quad (1)$$

where m is the weight of permeate passing through the effective membrane area (A) during time t . The compositions of the feed solution and permeate were analyzed by gas chromatography (HP6890, Agilent, USA). Then, the selectivity of the membrane (α_{ij}) was obtained as follows:

$$\alpha_{ij} = \left(\frac{w_i^p}{w_j^p} \right) \left(\frac{w_i^f}{w_j^f} \right)^{-1} \quad (2)$$

where w_k^p and w_k^f ($k = i$ or j) refers to the weight fraction of penetrants i (water) or j (ethanol) in the permeate and in the feed, respectively.

RESULTS AND DISCUSSION

Formation and structure of the waterborne PU/PVA membranes

Waterborne PU/PVA membranes were prepared through blending of waterborne PU and PVA with different ratios. APTES of different dosages (1.78, 3.36, and 4.97 wt %) was used as a modifier for waterborne PU. Because of the high reactivity of amine groups ($-\text{NH}_2$) toward the isocyanate groups ($-\text{NCO}$), APTES could be linked to the end of PU chains, which retarded the further growth of the PU chains. The alkoxy groups [$-\text{Si}(\text{OR})_3$ ']s from APTES then underwent the hydrolysis and condensation process to form the $-\text{Si}-\text{O}-\text{Si}-$ crosslinking, and hence, the polymer chains were expanded further, as illustrated in Scheme 1.

To investigate the membranes chemical and crystalline structures, FTIR and WXR D measurements were conducted, and some typical spectra are shown in Figures 1 and 2.

All of the FTIR spectra showed bands in the range 3300–3500, about 1710, and about 1550 cm^{-1} ; these bands were characteristic of the urethane groups ($-\text{NH}-\text{C}=\text{O}$ stretching and $-\text{N}-\text{H}$ formation vibration) from waterborne PU. From M1, M2, and M3 to M4, these three bands generally decreased because of the gradual decrease of waterborne PU content. A similar changing trend was observed in the spectra of M5–M8 and M9–M12. The peaks at about 1100 cm^{-1} were characteristic of $\text{C}-\text{O}-\text{C}$ and $-\text{Si}-\text{O}-\text{Si}-$ stretching,^{22,23} whereas the peaks at about 1465 cm^{-1} were from the stretching of $-\text{CH}_2-$ and $\text{CH}-$ groups (ν and δ). For membranes with different APTES dosages (M4, M8, and M12), the intensity of the band in the range of about 1100 cm^{-1} was similar. This should have been due to the overlapping of the $-\text{C}-\text{O}-\text{C}-$ group from PVA. The dosage of APTES was low, and hence, the intensity change could not be well distinguished.

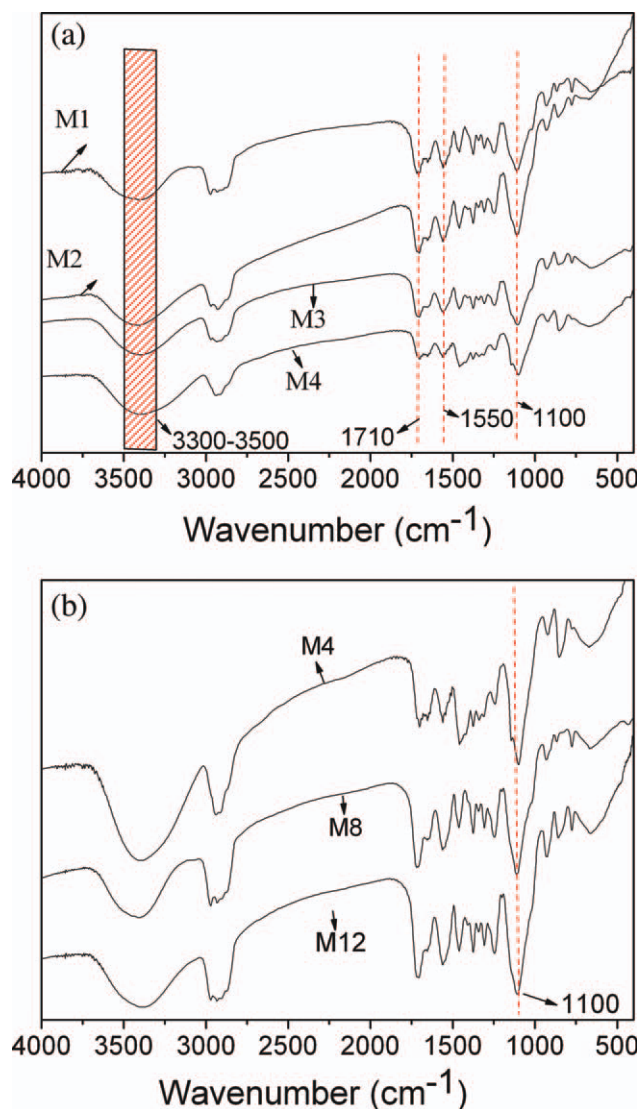


Figure 1 FTIR spectra of membranes (a) M1–M4 and (b) M4, M8, and M12. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

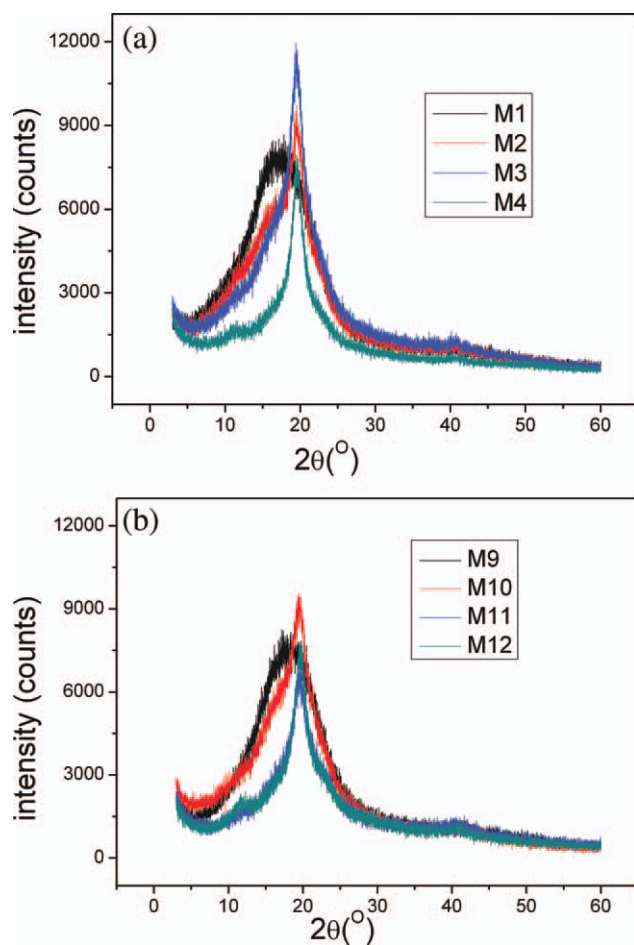


Figure 2 WXR D graphs of membranes (a) M1–M4 and (b) M9–M12. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 2, M1 showed a wide peak at $2\theta \approx 17^\circ$. The peak shifted to the right ($2\theta \approx 20^\circ$) and gradually became sharper from M1 to M4. From M9 to M12 or from M5 to M8, a similar trend was observed. Nevertheless, the peaks for M11 and M12 were wider compared to those of M3 and M4.

The intensity change of the WXR D peaks indicated the gradual increase of the crystallinity as the PVA content increased from M1 to M4, from M5 to M8, or from M9 to M12. Pure PVA showed a relatively sharp WXR D peak at $2\theta \approx 20^\circ$ because of the (101) plane.²⁴ M9–M12 contained a greater silica content than M1–M4. A silica network was formed after the sol–gel process. Therefore, the packing of polymer chains was more difficult, and the crystallinity became lower.²⁵

Thermal stability

TGA was conducted to investigate the thermal stability of the membranes. Some typical TGA diagrams are shown in Figure 3.

The decomposition temperature (T_d) values and the weight loss peaks were collected and are shown

in Table II. A comparison of the different TGA diagrams revealed the following conclusions:

1. For waterborne PU membranes without PVA blending [M1, M5, and M9; Fig. 3(a)], the weight loss peaks shifted to higher temperatures as the APTES dosage increased. Especially for M9, the first weight loss peak was at about 330°C ; this was higher than the values of M1 ($\sim 296^\circ\text{C}$) and M5 ($\sim 315^\circ\text{C}$). Hence, the thermal stability could be enhanced after the incorporation of APTES.
2. For the waterborne PU/PVA membranes, the first weight loss peak generally shifted to a lower temperature as the PVA dosage increased. Also, M4, M8, and M12, which contained the highest PVA content showed the lowest T_d values. Hence, the thermal stability decreased slightly as the PVA dosage increased; this should have been due to the lower stability of PVA compared with waterborne PU.¹⁹

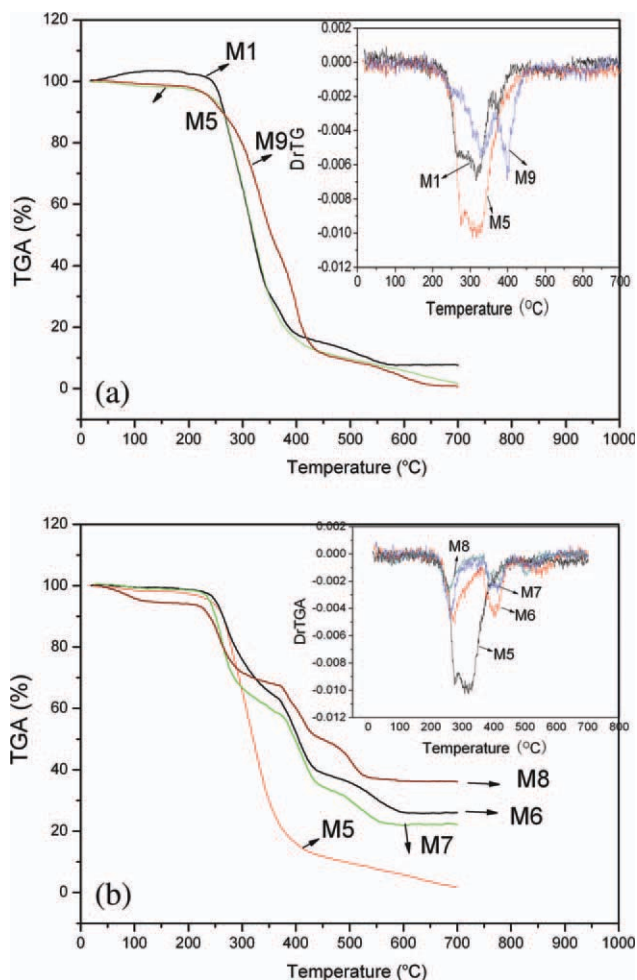


Figure 3 TGA and differential thermogravimetric (DrTGA) diagrams of the membranes (a) M1, M5, and M9 and (b) M5–M8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
T_d Values and Weight Loss Peaks of Membranes M1–M12

Membrane	<i>T_d</i> (°C) ^a	Weight loss peak		
		First	Second	Third
M1	250.1	296	377	—
M2	232.4	283	375	549
M3	250.5	294	404	576
M4	230.4	260	400	507
M5	252.1	311	—	—
M6	253.2	271	402	547
M7	242.4	262	400	518
M8	239.3	254	395	501
M9	243.3	330	398	—
M10	250.3	269	399	518
M11	247.4	265	413	525
M12	232.5	256	399	498

^a *T_d* is defined as the temperature of 5% weight loss.

Morphology of the hybrid membranes

The morphologies of the cross sections of the membranes were observed through SEM, and the micrographs of some typical examples are shown in Figure 4.

The membranes from waterborne PU were all compact and homogeneous, despite the different APTES dosages. Hence, APTES could be incorporated homogeneously in the waterborne PU matrix.¹⁰ When waterborne PU was blended with PVA, the membranes exhibited obvious phase separation. The aggregations were due to the waterborne PU particles, whereas PVA provided a continuous phase.¹⁹ A possible mechanism for the membrane morphology was found after we checked the membrane preparation process. During the waterborne PU emulsion preparation process, APTES was linked to the end of the PU prepolymer chains. The alkoxy-silane (—SiOR) groups were hydrolyzed to form the silanol groups (—SiOH). The —SiOH groups may have then undergone self-condensation or cocondensation with the —OH groups from PVA during the blending process or during the elaboration and heating processes. Self-condensation formed crosslinking between the waterborne PU chains, and hence, the aggregation was enhanced. This decreased the homogeneity with PVA chains. Cocondensation with the —OH groups of PVA, on the other hand, induced the crosslinking of PU with PVA. This increased the compatibility of the mixing system. Therefore, the competition between these two kinds of reactions were vital to the morphology of the final membranes, as illustrated in Figure 5.

In this study, TEA and EDA were used for the quaternization and chain-expansion processes, as shown in steps 3 and 4 of Scheme 1. TEA and EDA were both bases and, hence, could act as the catalyst for the condensation reaction of the —SiOH

groups.²⁶ Therefore, the self-condensation of the waterborne PU chains was enhanced. Experimental observations also showed that the waterborne PU emulsion with higher APTES dosages (3.36 and 4.97%) could not remain stable after a long period of preservation. Some deposition appeared after around 16 h; this should have been due to the crosslinking and aggregation of the waterborne PU chains. The mechanism, as discussed previously, was in accordance with previously reported results. For instance, in the work of Sardon et al.,¹⁰ no EDA

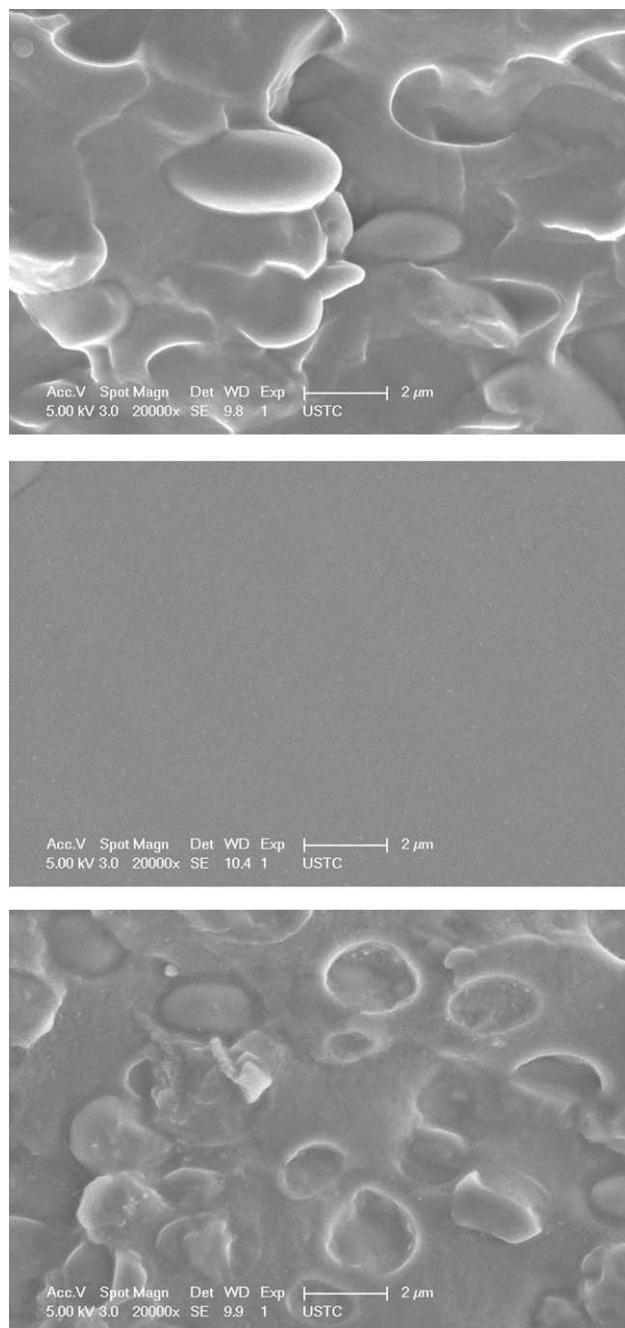


Figure 4 SEM graphs of the membrane cross sections (magnification of enlargement = 20,000).

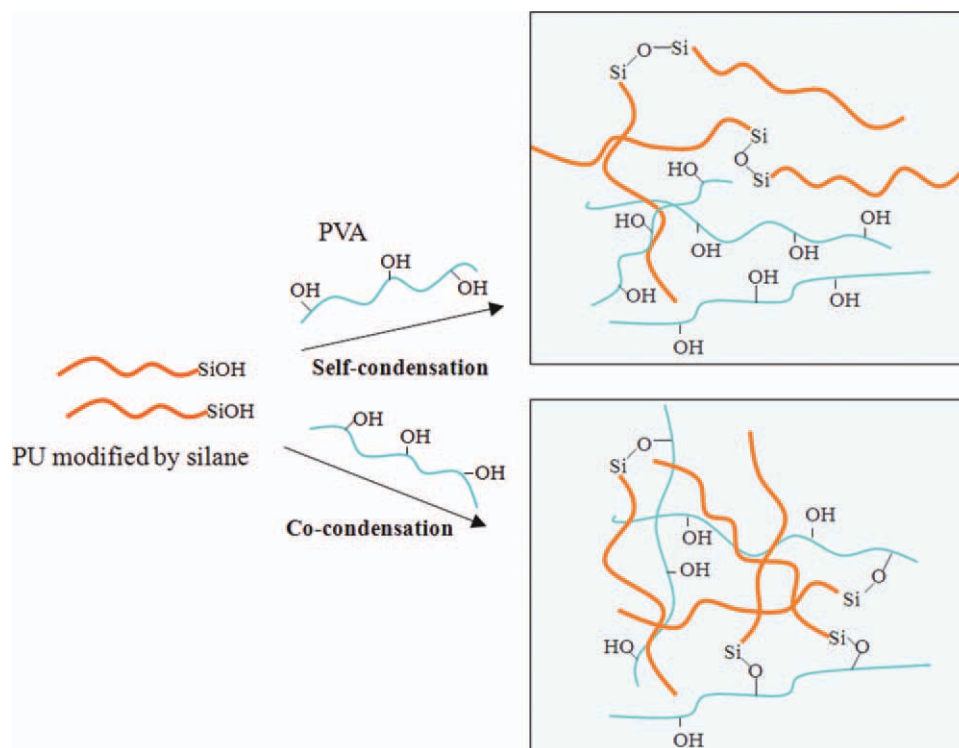


Figure 5 Illustration of the possible condensation processes between waterborne PU and PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was used, and TEA was added before the addition of APTES. In this way, waterborne PU with a better homogeneity was obtained.¹⁰

The mechanism, as illustrated in Figure 5, also gave clues for the further improvement of the waterborne PU/PVA membrane compatibility. For instance, TEA could be added before the addition of APTES, and EDA could be replaced by another chain expander. Also, some different silanes, such as γ -glycidoxypropyltrimethoxysilane, could be used. γ -Glycidoxypropyltrimethoxysilane could be linked to the side chains of waterborne PU. Hence, the growth of the PU chains was more developed, and the dosage of the chain expander (EDA) was decreased.

Swelling resistance in 40°C hot water or ethanol

Because PVA could be readily swollen or even dissolved in hot water, the stability of the membranes in water was a major concern. W_R , defined as the weight gain of the membranes in 40°C water for 2 days, was collected, and the results are shown in Table III.

For practical applications, such as pervaporation, the stability in organic solvents was also important. Hence, the membrane swelling performances in ethanol were conducted, and the obtained Et_R values are shown in Table III. M1 and M5 partially dissolved and became gel-like during the measurement. M2, M3, and M7 exhibited weight losses of 24.9, 5.0,

and 10.4%, respectively; this was probably due to the strong swelling and partial dissolving.

As the PVA content increased, the swelling of the membranes in water generally increased; this was due to the high hydrophilicity of the PVA chains. On the other hand, the swelling in ethanol was

TABLE III
 W_R and Et_R Values of the Membranes at 40°C

APTES (wt %) in waterborne PU	PVA (wt %) in the PVA + waterborne PU mixture	Membrane	W_R (%)	Et_R (%)
1.78	0	M1	43.0	— ^a
	33.3	M2	54.1	−24.9 ^b
	50.0	M3	62.7	−5.0 ^b
	66.7	M4	106.4	41.3
3.36	0	M5	8.6	— ^a
	33.3	M6	63.5	4.5
	50.0	M7	86.8	−10.4 ^b
	66.7	M8	84.3	0.2
4.97	0	M9	11.0	262.6
	33.3	M10	50.0	44.2
	50.0	M11	77.4	11.0
	66.7	M12	125.3	21.2

^a The data could not be obtained because the membranes partially dissolved and became gel-like during the measurements.

^b The data were negative because the membranes were strongly swollen and partially dissolved during the measurements.

significantly depressed as the PVA content increased. For instance, M1 (PVA dosage: = 0%) became gel-like when it was immersed in ethanol, whereas M4 (PVA dosage = 66.7%) retained integrity and showed a relatively low swelling degree of 41.3%. Therefore, the incorporation of PVA obviously enhanced the organic solvent resistance.

The dosage of APTES also had a strong influence on the membrane swelling behavior. As APTES increased, the swelling in water or ethanol generally followed a decreasing trend. For instance, M1 (APTES dosage = 1.78%) and M5 (APTES dosage = 3.36%) became gel-like in ethanol. M9 (APTES dosage = 4.97%) retained its integrity, although the swelling degree was high (262.6%). The swelling degree in water changed from 43.0 to 8.6 to 11.0% from M1 to M5 to M9.

Mechanical properties of the hybrid membranes

On the basis of the results of the mechanical testing, the following conclusions were thus obtained with regard to the influence of the PVA and APTES contents on the mechanical properties of the membranes:

1. With an increase in the PVA content, the TS values gradually increased (Fig. 6). When the APTES content was fixed at 1.78%, the TS value increased from 6.79 to 38.35 MPa as the PVA dosage increased from 0 to 66.7% (M1 to M4). Meanwhile, TS increased from 7.58 to 34.71 MPa or from 8.19 to 35.43 MPa when APTES was fixed at 3.36 or 4.97%. This was probably due to a higher stiffening effect of the relatively more rigid PVA polymer chains.¹⁹
2. With an increase in the APTES dosage, the TS values generally increased slightly at lower

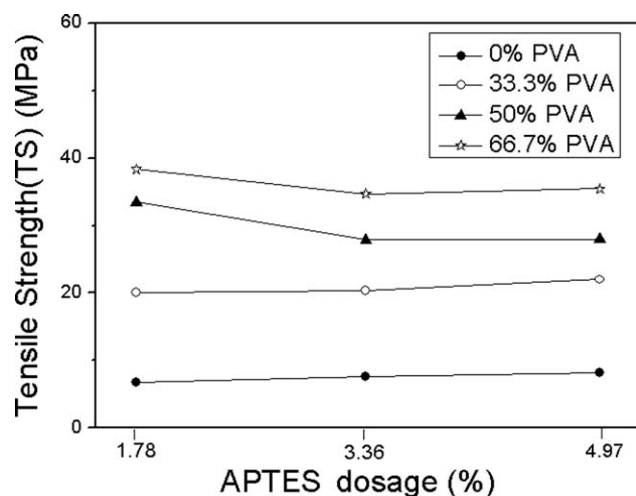


Figure 6 TS values of the membranes.

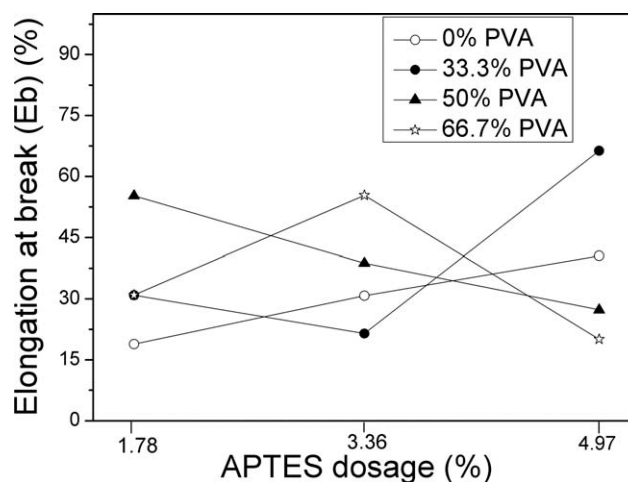


Figure 7 E_b values of the membranes.

PVA contents. For higher PVA dosages, TS decreased somehow when APTES was increased from 1.78 to 3.36% but then slightly increased with further increases in the APTES dosage to 4.97%.

3. The E_b values were in the range 18.9–66.3% (Fig. 7). For the waterborne PU membranes, the E_b values increased as the APTES dosage increased. Nevertheless, for the waterborne PU/PVA membranes, the influence of the PVA or APTES dosage on the E_b values was irregular, for which the membrane defects and phase separation may have been responsible. It is well known that membrane defects will significantly affect the membrane mechanical properties, especially the elongation results. In the waterborne PU/PVA membranes, the phase separation was obvious, and hence, defects were more likely to appear during the preparation procedures.

Pervaporation results

Among the different membranes, those with a higher content of PVA could resist ethanol better, and hence, we choose M4, M8, and M12 for the pervaporation operation. The results show that M4 showed the best separation performance. The separation factor (α) was 38.42, and the permeation flux was $128.0 \text{ g m}^{-2} \text{ h}^{-1}$. Compared with previous membranes based on PVA,¹⁵ the results here were comparable.

M8 and M12 showed very high flux values but no separation performance during the pervaporation experiments. The microphase separation, as discussed earlier, were probably responsible. As the APTES content increased from M4 to M8 to M12, the inorganic silica content increased and induced more

serious phase separation. Hence, ethanol and water could go through the membrane through the inter-phase areas.

CONCLUSIONS

Membranes were prepared from the blending of PVA with waterborne PU. APTES was used as the modifier. The membranes gradually became more crystalline as the PVA content increased. The swelling behavior in ethanol was significantly depressed as the PVA content increased. For instance, M1 (PVA dosage = 0%) became gel-like when it was immersed in ethanol, whereas M4 (PVA dosage = 66.7%) retained its integrity and showed a relatively low swelling degree of 41.3%. The strength and thermal stability increased as APTES increased. Nevertheless, the microphase separation increased at the same time.

The membranes were tried for ethanol/water mixture separation through pervaporation. α for M4 was 38.42, and the permeation flux was $128.0 \text{ g m}^{-2} \text{ h}^{-1}$. Therefore, membranes based on PVA and waterborne PU could be potentially used in pervaporation applications. Further improvement of the membranes is underway, and the results will be reported in the near future.

References

1. Yen, M. S.; Tsai, P. Y.; Hong, P. D. *Colloids Surf A* 2006, 279, 1.
2. Bai, C. Y.; Zhang, X. Y.; Dai, J. B.; Zhang, C. Y. *Prog Org Coat* 2007, 59, 331.
3. Yen, M. S.; Tsai, P. Y. *J Appl Polym Sci* 2003, 90, 233.
4. Jeon, H. T.; Lee, S. K.; Kim, B. K. *J Adhes* 2008, 84, 1.
5. Yen, M. S.; Tsai, P. Y. *J Appl Polym Sci* 2006, 102, 210.
6. Chen, J. J.; Zhu, C. F.; Deng, H. T.; Qin, Z. N.; Bai, Y. Q. *J Polym Res* 2009, 16, 375.
7. Pan, H. X.; Chen, D. J. *Eur Polym J* 2007, 43, 3766.
8. Zhao, B.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Zeng, W.; Rong, M. Z.; Zheng, Q. *J Mater Sci* 2007, 42, 4575.
9. Yen, M. S.; Tsai, H. C.; Hong, P. D. *J Appl Polym Sci* 2006, 100, 2963.
10. Sardon, H.; Irusta, L.; Fernández-Berridi, M. J.; Lansalot, M.; Bourgeat-Lami, E. S. *Polymer* 2010, 51, 5051.
11. Wu, C. M.; Wu, Y. H.; Luo, J. Y.; Xu, T. W.; Fu, Y. X. *J Membr Sci* 2010, 356, 96.
12. Binsu, V. V.; Nagarale, R. K.; Shahi, V. K. *J Mater Chem* 2005, 15, 4823.
13. Kim, D. S.; Park, H. B.; Rhim, J. W.; Lee, Y. M. *Solid State Ionics* 2005, 176, 117.
14. Zhang, Q. G.; Liu, Q. L.; Chen, Y.; Chen, J. H. *Ind Eng Chem Res* 2007, 46, 913.
15. Zhang, Q. G.; Liu, Q. L.; Jiang, Z. Y.; Chen, Y. *J Membr Sci* 2007, 287, 237.
16. Wu, Y. H.; Wu, C. M.; Li, Y.; Xu, T. W.; Fu, Y. X. *J Membr Sci* 2010, 350, 322.
17. Yang, J. M.; Chiang, C. Y.; Wang, H. Z.; Yang, C. C. *J Membr Sci* 2009, 341, 186.
18. Kumar, M.; Shalini, V. K. S. *J Phys Chem B* 2010, 114, 198.
19. Yun, J. K.; Yoo, H. J.; Kim, H. D. *Macromol Res* 2007, 15, 22.
20. Chen, J.; Huang, J. Q.; Li, J. D.; Zhan, X.; Chen, C. X. *J Chem Eng Jpn* 2009, 42, 640.
21. Zhang, Q. G.; Liu, Q. L.; Jiang, Z. Y.; Ye, L. Y.; Zhang, X. H. *Micropor Mesopor Mater* 2008, 110, 379.
22. Wu, Y. H.; Wu, C. M.; Gong, M.; Xu, T. W. *J Appl Polym Sci* 2006, 102, 3580.
23. Innocenzi, P. *J Non-Cryst Solids* 2003, 316, 309.
24. Shao, C. I.; Kim, H. Y.; Gong, J.; Ding, B.; Lee, D. R.; Park, S. J. *Mater Lett* 2003, 57, 1579.
25. Kim, D. S.; Park, H. B.; Rhim, J. W.; Lee, Y. M. *J Membr Sci* 2004, 240, 37.
26. Pierre, A. C. *Introduction to Sol-Gel Processing*; Kluwer Academic: Boston, 1998.