Pervaporation separation of ethanol/water mixture using modified zeolite filled PDMS membranes

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ABSTRACT: In this article, the composite polydimethylsiloxane (PDMS) membranes supported by cellulose acetate (CA) microfiltration membrane were successfully prepared by adding modified zeolite particles with a silane coupling agent, $NH_3–C_3H_6–Si(OC_2H_5)_3$. The sorption and diffusion behaviors of ethanol and water in the films were studied. The results showed that with the increase in the modified zeolite content, the solubility selectivity increased, but the diffusion selectivity first increased, then decreased. The effects of modified zeolite content and feed temperature on the pervaporation performance of the composite membranes in 10 wt % ethanol/water mixture were also investigated. When modified zeolite loading was 20 wt %, for 10 wt % ethanol/water mixture at 40°C, the permeate flux was 348.7 $g \cdot m^{-2} \cdot h^{-1}$, the separation factor was 14.1, and the permeate separate index was 4568, respectively. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41897.

INTRODUCTION

Because of the escalating demand and depleting supply of conventional resources, i.e., fossil fuels, it is imperative to develop sustainable alternative resources to alleviate humankind's reliance on petroleum and to reduce the environmental pollution from fossil fuel combustion. The application of biomass into an energy source by the fermentation process to produce bioethanol has progressively gained more attention from governments worldwide in recent years.[1,2]

Traditional fermentation is an attractive technique for producing ethanol directly. However, it is known that the process is seriously inhibited by ethanol itself. As a consequence, rather low ethanol concentration is obtained in the final fermentation broth. One approach to relieve such negative impact on the productivity of ethanol is to remove ethanol from the fermentation broth consecutively. At present, membrane pervaporation integrated with a bioreactor plays a dominant part in realizing continuous fermentation because of its energy-saving, cost-effective, and environmentally friendly qualities as well as the fact that it has no negative influence on the microorganisms.[3–5]

Many hydrophobic polymer and inorganic membrane materials have been researched for removing ethanol from aqueous solution. Among them, polydimethylsiloxane (PDMS) has been the most popular material.[6–9] The incorporation of zeolite particles into PDMS matrix has been shown to enhance the separation

performance for ethanol/water mixture. Adnadjevic et al.[10] determined the pervaporation properties of PDMS membranes filled with several kinds of hydrophobic zeolites. An increase in the zeolite content resulted in an increase in both the membrane permeability and selectivity, but the flux was still low. Bowen et al.[11] prepared some sandwich-type PDMS composite membranes which included a pure PDMS top coat, a ZSM-5 zeolite/PDMS middle layer and an UF membrane support layer. They found that when 65% ZSM-5 zeolite/PDMS was prepared as the middle layer, twice of the flux and separation factor were obtained when compared with the pure PDMS membrane, which were up to 521 $g \cdot m^{-2} \cdot h^{-1}$ and 18, respectively. Dobrak et al.[12] also observed a significant increase in the selectivity for PDMS membrane filled with commercial CBV 3002 fillers. However, it seems to be difficult to obtain well-dispersed inorganic-organic nanocomposite membranes duo to the strong tendency of aggregation of inorganic nanoparticles. Therefore, it is necessary to prepare well-dispersed inorganic–organic nanocomposite membranes and apply them to concentrate organic components from dilute ethanol solution by pervaporation. Zhou el al.[13] treated the nano-sized silicalite-1 with a silane coupling agent vinyltriethoxysilane (VTES) and incorporated it into PDMS matrix for the pervaporation of dilute ethanol solutions. The results showed that VTES could enhance the separation factor of the membrane by improving the compatibility between the silicalite-1 and PDMS matrix. Sun et al.[14] used a silane coupling agent, 3-mercaptopropyltrimrthoxysilane
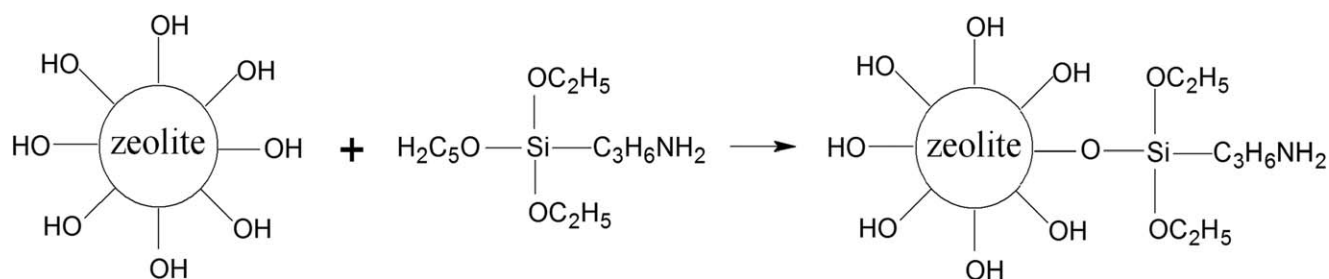
Scheme 1. Schematic representation of the silanization mechanism of zeolite particles.

(MPTMS), to modify the surface property of H-ZSM-5. It was found that with the increase in surface-modified ZSM-5 content, the number of nonselective voids in the filled membrane decreased, and the pervaporation performance was improved. Liu et al.[15] prepared a stable PDMS/ZSM-5 zeolite composite layer on a tubular ceramic support by using n-octyltriethoxysilane (OTES) to graft ZSM-5 zeolite with the particle size of 4.9 μm. For 5 wt % ethanol solution at 40°C, the total flux of the ceramic-supported composite membrane reached 408 g m^{-2} h^{-1}, and the separation factor was 14.

In this article, the zeolite particles were modified with a silane coupling agent, $NH_3–C_3H_6–Si(OC_2H_5)_3$ (KH-550), and were incorporated into PDMS matrix to form the mixed matrix membranes. The sorption and diffusion behaviors of water and ethanol were measured. The effects of preparation conditions and operation conditions on the pervaporation performances of the composite membranes for 10 wt % ethanol/water mixture were also investigated.

EXPERIMENTAL

Materials
Polydimethylsiloxane (PDMS, RTV 107) was purchased from Chengguang Chemical Institute (Chengdu, China). The silane coupling agent γ-Aminopropyltriethoxysilane ($NH_3–C_3H_6–Si(OC_2H_5)_3$, KH-550) was chemically pure and obtained from Shanghai Yaohua Chemical Plant (Shanghai, China). Crosslinking agent tetraethylorthosilicate ($Si(OEt)_4$, TEOS), catalyst dibutyltin dilaurate and solvent n-hexane were obtained as analytical reagents from Tianjin Chemical Reagent Co. (Tianjin, China). Cellulose acetate (CA) microfiltration membrane with an average pore size of 0.45 μm was purchased from Shanghai Xinya Purification Instruments (Shanghai, China). Zeolite (ZSM-5, Si/Al = 300, diameter = 200 nm, BET surface area = 300 m^{-2}·g^{-1}, and average pore size = 5 Å) was purchased from Nankai University Catalyst Co. All the reagents were used without further purification.

Surface Modification of Zeolite Particles
Raw zeolite of 5 g and 20 mL of n-hexane were added into a container, which was magnetically stirred for 30 min and then under untrasonication for 20 min to disperse the zeolite particles sufficiently. Next, 2.5 g KH-550 was added into the suspension and stirred for another 30 min. And then the suspension was centrifuged and rinsed with n-hexane to remove the residual KH-550. All the filter cake was dried at 100°C for 5 h to evaporate the adsorbed n-hexane. The mechanism of the

modification was illustrated in Schemes 1 and 2. The oxyethyl group of silane coupling agent reacted with the hydroxyl of zeolite forming siloxane bridges. Then the unreacted oxyethyl group of the modified zeolite may continue to react with the hydroxyl of PDMS.

Membrane Preparation
The PDMS membranes were prepared by solution casting method. PDMS and crosslinking agent were dissolved in n-hexane. After the mixture was stirred for 2 h, the catalyst was added in the solution. The mass ratio of PDMS, crosslinking agent and catalyst was 10 : 1 : 0.2. The solution was mixed for an additional 30 min. The solution was then sonicated for 30 min to remove air bubbles. The homogeneous solution was cast onto a Teflon (PTFE) plate or a CA support membrane which has been pretreated with water. The film or the composite membrane was dried in a vacuum oven at 60°C for 6 h to assure complete crosslinking.

For the preparation of 10 wt %, 20 wt %, 30 wt %, 40 wt %, and 50 wt % zeolite filled PDMS membranes, the zeolite particles were added in the solution before the addition of the catalyst. After mixing for 1 h, the catalyst was added in the solution. The rest of the preparation process was just as the same as that of unfilled membranes.

Zeolite and Membrane Characterization
Fourier Transform Infrared. Fourier transform infrared (FT-IR) spectra of the samples were recorded for the silane coupling agent, zeolite particles and modified zeolite particles at a scanning range of 400–4000 cm^{-1} using a FT-IR Spectrum 400 spectrometer (PE). The solid samples were ground well with KBr to make pellets.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was used to examine the particle morphology of the zeolite and the surface and cross-section structure of the prepared composite membranes. For the analysis of the cross-section morphology, the samples were first fractured in liquid nitrogen before measurement. Then the surface and fractured section were coated with a conductive layer of sputtered gold. The instrument used was a XL30 scanning electron microscopy (FEA).

Thermal Gravimetric Analysis. The thermal gravimetric analysis (TGA) was performed using a Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer (MA). The sample was heated from room temperature up to 800°C at a heating rate of 10°C min^{-1} in
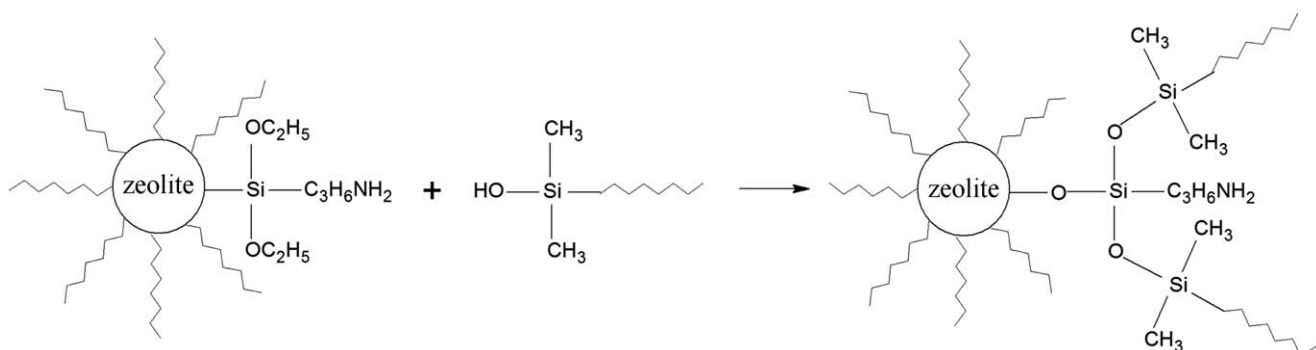
Scheme 2. Schematic representation of the further reaction mechanism in PDMS.

nitrogen, with a flow rate of 20 mL min^{-1}. All thermal degradation data were obtained from the TGA curves.

Contact Angle Analysis. The contact angle of water on the surface of the composite membrane was measured by a contact angle device at room temperature. The angles of sessile drops were analyzed using the system software 5 s later.

Swelling Experiment
Swelling degree (SD) is an important parameter to understand the interaction between the membranes and the penetrates. The dried samples without support were cut into 30 mm × 50 mm specimens. The weight and thickness of the dried films were measured. Then the dried films were immersed in 10 wt % ethanol/water mixture, pure ethanol or water at 40°C. After a fixed time interval, the films were removed from the solvents and wiped with tissue paper and were weighed immediately. The equilibrium solvent uptake was measured until no significant weight increase was observed for the swollen films. Four to five measurements were performed. The average swelling degree of the active layer of the composite membrane was calculated by using the following equation:

$$SD = \frac{W_s - W_d}{W_d} \times 100\% \tag{1}$$

where W_s and W_d are the weights of fully swollen and dried films, respectively. The sorption selectivity (α_s) was calculated by the following equation:[16]

$$\alpha_s = \frac{W_{E,\infty}}{W_{W,\infty}} \tag{2}$$

where $W_{E,\infty}$ and $W_{W,\infty}$ are the equilibrium solvent uptakes for pure ethanol and water, respectively. The diffusion coefficients of ethanol and water in the active layer of the composite membrane were calculated from the initial linear parts of the sorption curves obtained through the following equation:[17]

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D_t}{L^2} \tag{3}$$

where M_t is the mass sorbed in the film at time t, M_∞ is the mass sorbed at equilibrium state, L is the initial thickness of the film, and D is the diffusion coefficient of the component diffused into the film. The diffusion coefficients of ethanol and water were calculated from the slopes of plots of the left-hand versus time according to the above equation. The diffusion selectivity (α_D) was calculated by the following equation:
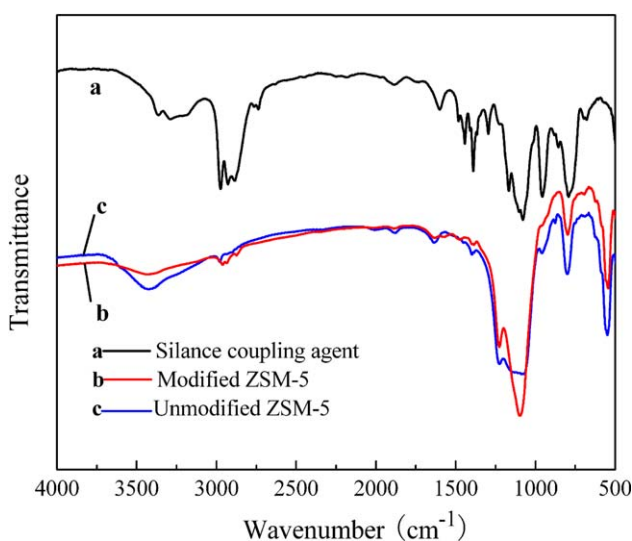
Figure 1. FT-IR spectra of the silane coupling agent, unmodified and modified zeolite particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
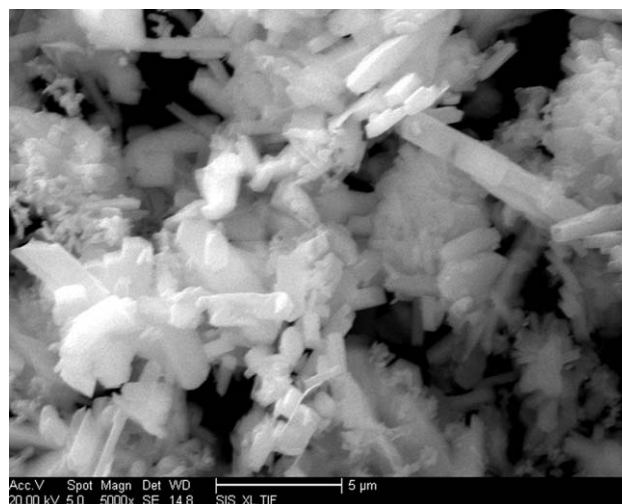
Figure 2. Morphology of zeolite particles.
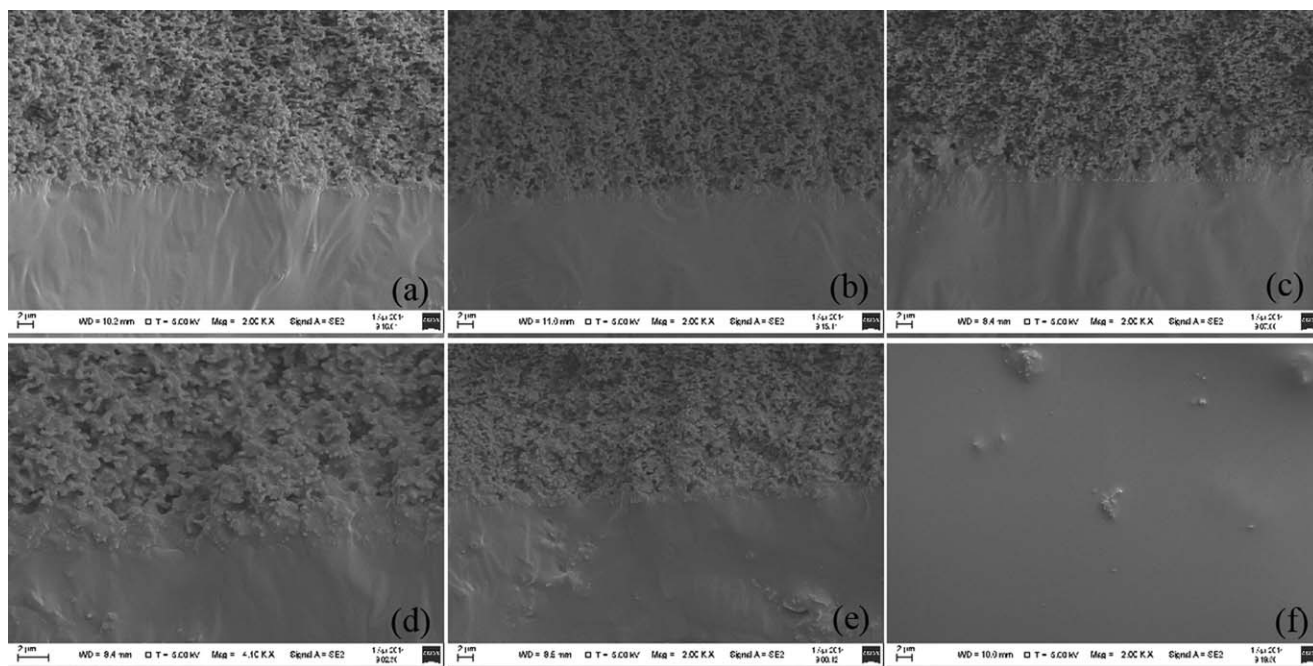
Figure 3. SEM photographs of modified zeolite filled PDMS/CA composite membranes: (a)–(e) cross-section morphology of 10%, 20%, 30%, 40%, and 50% modified zeolite filled PDMS/CA composite membranes (The upper layer is the support layer, and the lower layer is the separation layer); (f) surface morphology of 20% modified zeolite filled PDMS/CA composite membrane.

$$\alpha_D = \frac{D_E}{D_W} \tag{4}$$

where D_E and D_W refer to the pure ethanol and water diffusion coefficients, respectively.

Pervaporation Performance and Long-Term Stability of Composite Membranes

The pervaporation apparatus was same as used in our previous work.[18] 10 wt % ethanol/water mixture was used as the feed at 40°C. The pervaporation performances of the composite mem-

branes were characterized in terms of flux (J), separation factor (α), and permeate separate index (PSI), which are defined as:

$$J = \frac{Q}{At} \tag{5}$$

$$\alpha = \frac{y/(1-y)}{x/(1-x)} \tag{6}$$

$$PSI = (\alpha - 1)/J \tag{7}$$

where Q is the weight of the permeation (g), A is the effective membrane area (m^2), t is the operation time (h), and x and y are the concentrations of the components in the feed and permeation, respectively. Liquid nitrogen trap was use to collect
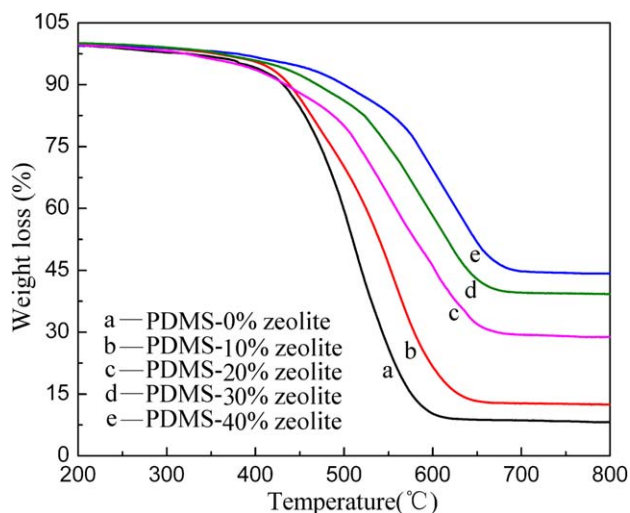
Figure 4. TG curves of modified zeolite filled PDMS films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
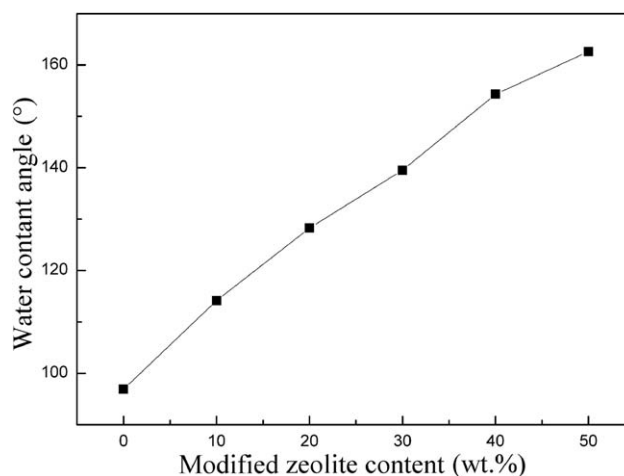
Figure 5. Water contact angle on the surface of modified zeolite filled PDMS membranes.
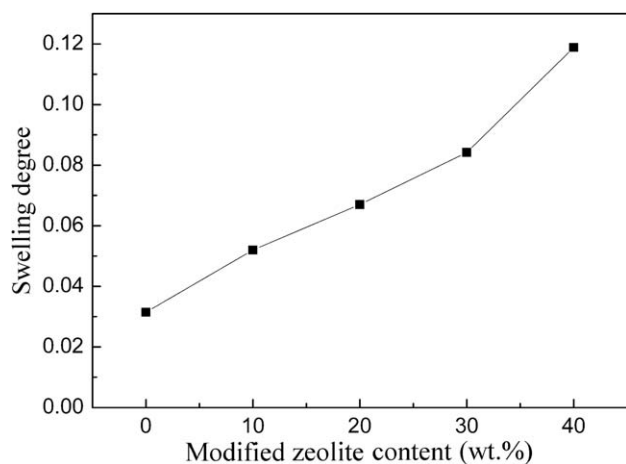
Figure 6. Swelling degree of the active layers of the composite membranes with different modified zeolite content.

Figure 8. Water uptake in the films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
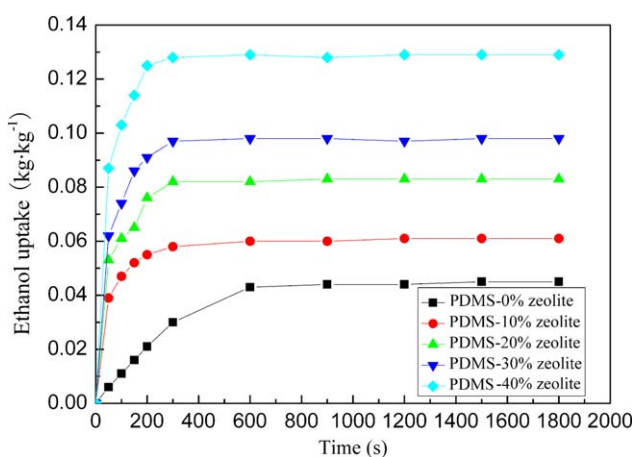
the permeation, and the concentration of collected ethanol was analyzed by an Abbe refractometer (WAY-2W, China). For the test of long-term stability, the total operation time is 7 days, and the permeation samples were analyzed for every 24 h.
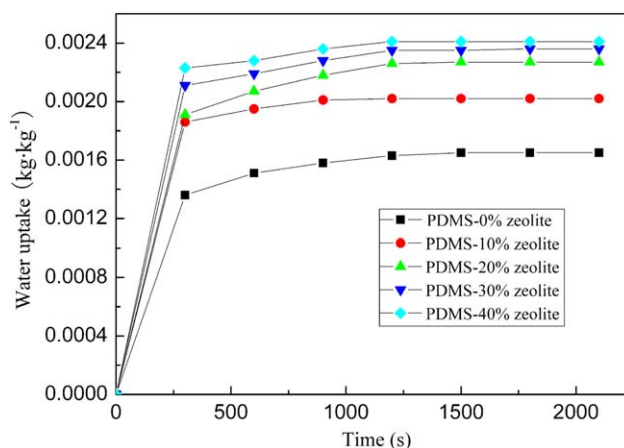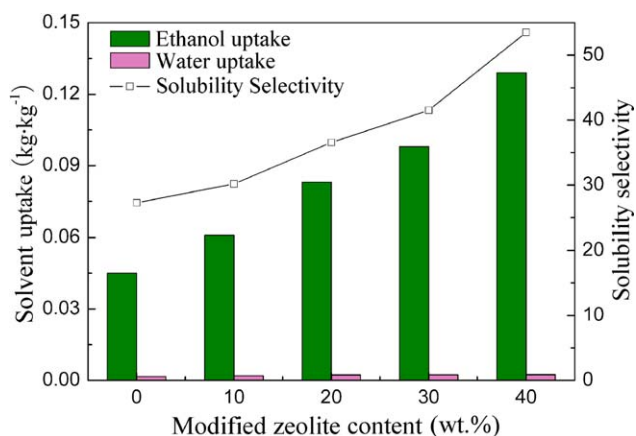
RESULTS AND DISCUSSION

Zeolite and Membrane Characterization
FT-IR Analysis. Figure 1 shows the FT-IR spectra of the silane coupling agent, unmodified and modified zeolite particles. As exhibited in Figure 1, the –OH stretching at 3370–3480 cm^{-1} becomes weaker for the modified zeolite when compared with the original peaks. The peaks at 2850–3000 cm^{-1} are related to the stretching of –CH$_2$ and –CH$_3$. Additionally, a sharp characteristic peak of the Si-O at 1081 cm^{-1} can be observed for the modified zeolite. Therefore, it demonstrates that KH-550 had reacted with –OH of ZSM-5 zeolite successfully.

SEM Analysis. Figure 2 shows the morphology of the zeolite particles. A cuboid crystal structure is observed for this zeolite. In order to investigate the distribution of the modified zeolite particles in the filled composite membranes, the morphologies of the cross-section of 0–50 wt % modified zeolite filled com-

posite membranes and the surface of 20 wt % modified zeolite filled composite membrane were analyzed.

As shown in Figure 3, the composite membranes were dense with no obvious defects and the modified zeolite particles dispersed uniformly in the PDMS matrix due to the good compatibility between the modified zeolite particles and PDMS. The active layer was tightly adhered on the surface of the CA support layer. From the surface morphology of the composite membrane, the modified zeolite particles did not exist obvious aggregation.

Thermal Gravimetric Analysis. Figure 4 shows the TG curves of the active layer of the composite membranes. As observed in the figure, the films filled with different content of zeolite showed a similar one-stage degradation, which suggested that the PDMS matrix was well mixed with the zeolite. In addition, it is evident that the addition of modified zeolite improved the stability of PDMS composite membranes. The decomposition temperature increased from about 425°C for the pure PDMS to about 468°C for 40 wt % zeolite filled PDMS membrane. Interestingly, all of the thermal decomposition temperatures were

Figure 7. Ethanol uptake in the films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Effect of modified zeolite content on the solubility selectivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
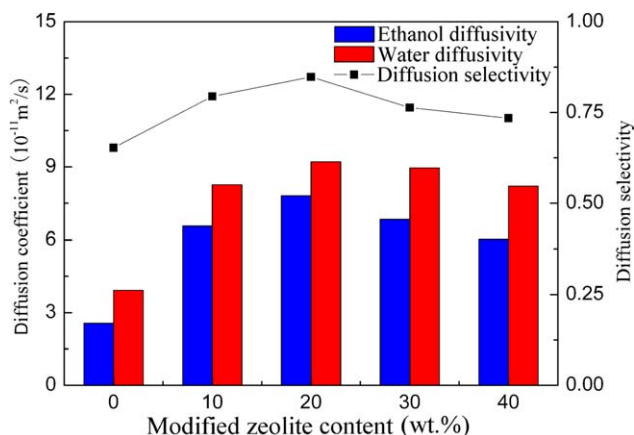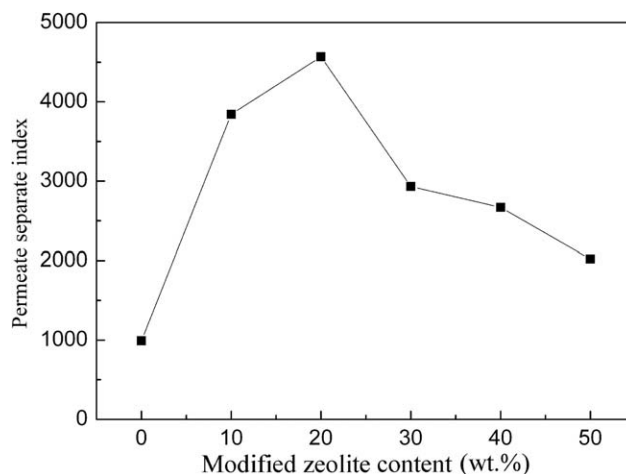
Figure 10. Effect of modified zeolite content on the diffusion selectivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 12. Effect of modified zeolite content in composite membranes on permeate separate index.

postponed for the zeolite filled PDMS membranes. This may due to the presence of the modified zeolite particles helped to adsorb the thermal energy and thus protected PDMS matrix from thermal attack.

Contact Angle Analysis. Figure 5 shows the water contact angle for the modified zeolite filled composite membranes. It can be seen that the water contact angle increased with the increase in modified zeolite content in the composite membranes, which suggested that the more modified zeolite content in the filled PDMS membranes, the higher hydrophobicity of the membrane surface. When the modified zeolite content increased from 0 wt % to 50 wt %, the water contact angle on the surface of the filled membranes increased from 96.9° to 162.6°.

Swelling Analysis
Swelling degree of the active layers of the composite membranes with different modified zeolite content in 10 wt % ethanol/water mixture at 40°C for 2 days were presented in Figure 6. It can be seen that the incorporation of modified zeolite into the

films enhanced the swelling degree and the swelling degree of these films increased with the increase in modified zeolite content. This may be due to that the physical incorporation of modified zeolite particles can interfere the packing structure of PDMS chains, which enhanced the accessible free volume in the matrix and in turn facilitated the sorption of water and ethanol molecules. A similar effect was observed by Sun et al.,[19] who used ONS-filled PDMS membranes to study the sorption behavior in 5 wt % ethanol aqueous solution at 40°C.

The typical sorption histories of pure ethanol and water in the active layers of the composite membranes at 40°C are shown in Figures 7 and 8, respectively. The equilibrium ethanol and water uptakes in the pure PDMS film were 0.045 kg·kg^{-1} and 1.72×10^{-3} kg·kg^{-1}, respectively. Ethanol was preferentially sorbed into PDMS over water due to the greater compatibility between ethanol and PDMS matrix. Ethanol has a solubility parameter of 26 MPa$^{0.5}$,[20] which is closer to that of PDMS (14.9 MPa$^{0.5}$) than that of water (49 MPa$^{0.5}$). When 20 wt %
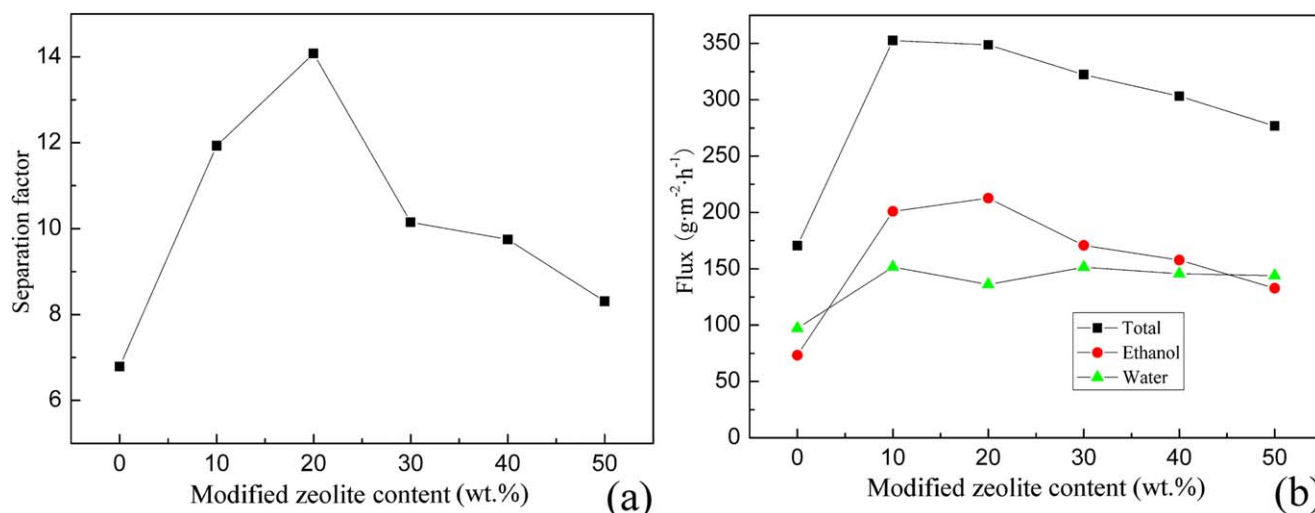
Figure 11. Effect of modified zeolite content in composite membranes on separation factor (a) and flux (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Comparison of Ethanol–Water Separation Performances of PDMS Membranes with Different Fillers

| Fillers	Content (wt %)	Feed concentration (wt %)	Temperature (°C)	Separation factor	Flux (g·m^{-2}·h^{-1})	Reference
Zeolite	60	5	22.5	16.5	51	22
USY	50	5	30	16.1	610 L·m^{-2}·h^{-1}	10
ZSM-5	50	5	30	14	460 L·m^{-2}·h^{-1}	10
APLO-5	50	5	30	5.2	200 L·m^{-2}·h^{-1}	10
Carbon black	4.5	13.7	20	10.1	127.32	23
Carbon black	10	6	35	9	49.8	24
Fumed silica	20	5	40	7	-	25
Nano-silica	5	5	60	30.1	114	19
ZSM-5	30	6	35	5	250	26
Zeolite Y	30	6	35	4.5	750	26
Silicalite-1	30	6	35	~10	350	26
Silicalite-1	77	7	22	59	71	27
Silicalite-1	65	5	50	43.1	-	28
Silicalite-1	50	5	50	12.2	120	29
ZSM-5	20	10	40	14.1	348	This work

modified zeolite was incorporated into the composite membrane, the ethanol and water uptakes in the composite membrane were 0.083 kg·kg^{-1} and 2.27×10^{-3} kg·kg^{-1}, respectively.

The effects of the modified zeolite content on the solubility selectivity and diffusion selectivity for pure ethanol over water at 40°C are shown in Figures 9 and 10, respectively, which can help to understand the following pervaporation performances. With the increase in the modified zeolite content, the ethanol uptake increased due to the promoted hydrophobicity caused by the incorporation of modified zeolite into PDMS and the water uptake increased very slowly. The increase in ethanol uptake may be due to the contribution from the water filling in the zeolite pore channel, which was similar to a capillary condensation mechanism.[21] Both ethanol and water diffusion

coefficients firstly increased then decreased with the increase in modified zeolite content in PDMS. This may be due to that when the modified zeolite content was below 20 wt %, the loose packing structure of PDMS chains caused by the incorporation of the zeolite was the main control factor for diffusion, but when the modified zeolite content was above 20 wt %, the main control factor may be the long and tortuous pore path caused by the big surface area and pore structure of the zeolite. When the modified zeolite addition was increased from 0 wt % to 20 wt % in PDMS, the solubility selectivity and diffusion selectivity exhibited the same trend which increased from 27.3 to 36.6 and from 0.65 to 0.85, respectively. When the modified zeolite addition was above 20 wt %, the solubility selectivity and diffusion selectivity presented opposite trends. These data
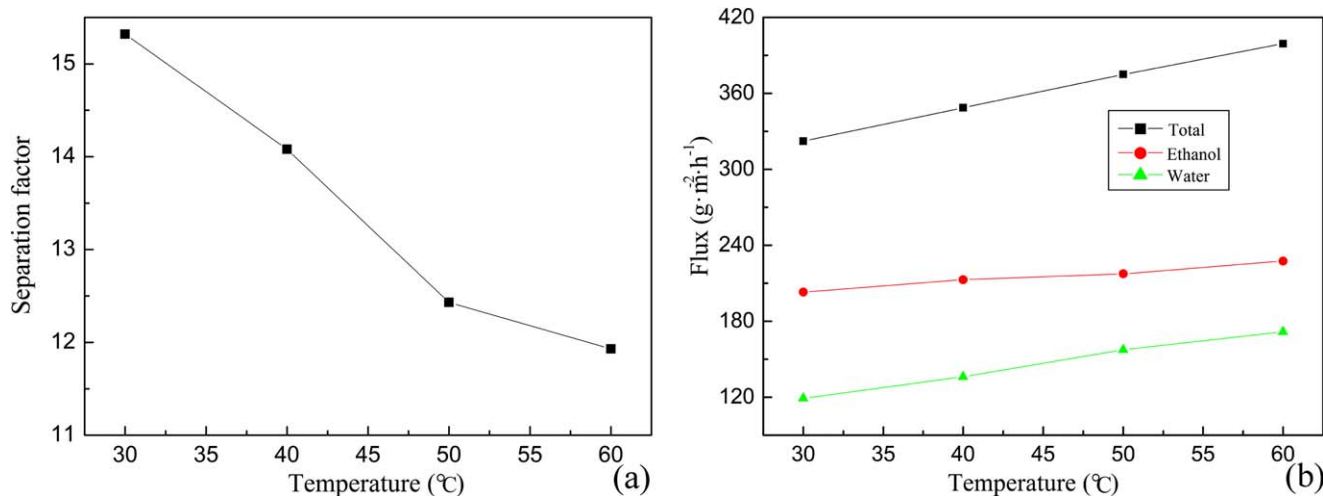
Figure 13. Effect of feed temperature on separation factor (a) and flux (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
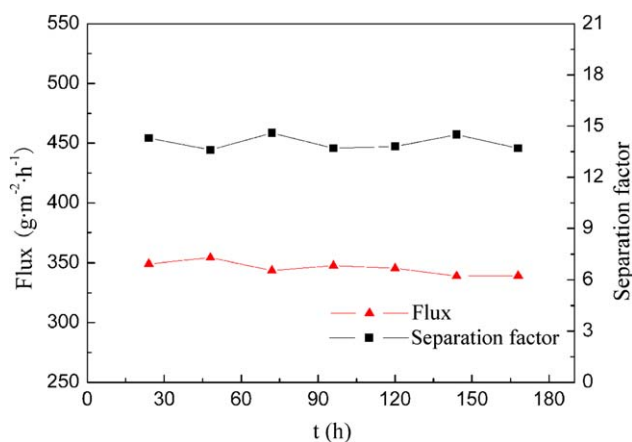
Figure 14. Effect of operation time on pervaporation performance of 20% modified zeolite filled PDMS/CA composite membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

suggested that the modified zeolite filled PDMS membranes preferentially favored to the sorption and diffusion of ethanol, which was desirable for concentrating ethanol from aqueous solution.

Pervaporation Performance

Effect of Modified Zeolite Content on Pervaporation Performance. Figures 11 and 12 show the effects of modified zeolite content in the composite membranes on the flux, separation factor and permeate separate index for 10 wt % ethanol/water mixture at 40°C. It can be seen that the membranes with moderate addition of modified zeolite exhibited remarkable advantages in the flux and separation factor. A similar effect was observed by Adnadjević et al.[10] that the addition of the three investigated types of hydrophobic zeolites resulted in an increase in membrane permeability and selectivity.

Figure 11(b) also clearly shows that with the increase in the modified zeolite content from 0 wt % to 50 wt %, the total flux first increased to the maximum when the modified zeolite content was 20 wt % then decreased slowly, the similar trend was also observed for silica filled membrane.[18] The separation factor increased from 8.3 to 14.1. The reason may be that the modified zeolite addition interfered with the tight packing of PDMS chains, which made the diffusion of the permeate molecules through the filled membranes easier. But the adsorption and diffusion rates of ethanol molecules increased more rapidly than that of water molecules, which were revealed by the swelling experiments. With the further increase in the modified zeolite content in the membranes, the flux decreased for the reason that the mesoporous structure of the zeolite made the permeate path to be long and tortuous. The decline of the separation factor when the zeolite content exceeded 20 wt % might be due to the excessive zeolite inhabited the free volume of cavities. Consequently, a balance between the above two competitive effects might cause the final result. Additionally, we introduced permeate separate index to analyze the pervaporation performance of the modified zeolite filled membrane. As shown in Figure 12, the permeate separate index presents the similar trend with the total

flux and the membrane filled with 20 wt % modified zeolite exhibits the best pervaporation performance in the experiment.

A comparison of ethanol–water separation performances of PDMS membranes with different fillers reported in the literatures is shown in Table I. It can be seen that the separation factor varied from 4.5 to 59. This may be due to the different preparation conditions adopted (e.g., loading, source and size of the particles, source of the PDMS and membrane casting conditions).[10,30] The separation factors and fluxes in the present work were not the highest, but a good comprehensive performance was obtained.

Effect of Feed Temperature on Pervaporation Performance. Figure 13 presents the effect of feed temperature on the pervaporation performance of 20 wt % modified zeolite filled composite membrane for 10 wt % ethanol/water mixture. As can be seen that with the increase in the operation temperature from 30°C to 60°C, the total flux increased, but the separation factor decreased slightly. This result was due to that the thermal motion of PDMS chains intensified with increasing temperature, which resulted in an expansion of the free volume. Consequently, the molecular diffusion was easier as the temperature increased, which led to the increase in the permeation flux. As for the separation factor, it presented an opposite trend to the flux as reported in the literatures.[10,29] The reason may be that the decrease in the cluster of water and the increase in the free volume of PDMS with the increasing temperature made the diffusion of water to be more easier. Furthermore, the increase in free volume was more effective on the diffusion of water molecules for its smaller molecular size.

Long-Term Stability of the Composite Membrane. The long-term stability of the composite membrane with 20 wt % modified zeolite in 10 wt % ethanol/water mixture at 40°C is shown in Figure 14. As can be seen from the figure, the permeation flux decreases slightly, while the separation factor of the composite membrane presents a low fluctuation. It demonstrated that, in spite of the swelling of the active layers, the separation performance of the composite membrane would not be influenced severely.

CONCLUSIONS

In this study, the mixed matrix membranes using modified zeolite filled PDMS as the top active layer and cellulose acetate (CA) microfiltration membrane as the support layer were prepared for the pervaporation of ethanol from water. NH_3–C_3H_6–$Si(OC_2H_5)_3$ (KH-550) was used as silane coupling agent to modify the surface property of the zeolite to enhance the compatibility between the particles and PDMS matrix. SEM graphs presented that the composite membranes were dense with no obvious defects. The modified zeolite particles uniformly dispersed in the PDMS matrix and the top layer was tightly adhered on the surface of the support layer. The swelling degree of the films in 10 wt % ethanol/water mixture enhanced with the modified zeolite content increasing. When the modified zeolite addition was increased from 0 wt % to 20 wt % in the PDMS matrix, the solubility selectivity and diffusion selectivity exhibited the same trend which increased from 27.3 to 36.6 and

from 0.65 to 0.85, respectively. Incorporation of modified zeolite into PDMS matrix could significantly influence the pervaporation performance of the PDMS membranes in 10 wt % ethanol/water mixture. When the modified zeolite loading was 20 wt %, for 10 wt % ethanol/water mixture at 40°C, the permeate flux was 348.7 $g \cdot m^{-2} \cdot h^{-1}$, the separation factor was 14.1, and permeate separate index was 4568, respectively. In addition, the modified zeolite filled PDMS/CA composite membranes showed good long-term stability.

ACKNOWLEDGMENTS

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