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Effects of PES support layer structure on pervaporation performances of PDMS/PES hollow fiber composite membranes

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ABSTRACT

Polyethersulfone (PES) hollow fiber ultrafiltration (UF) membranes were fabricated by the dry/wet-spinning method; hydrophobic PDMS/PES composite membranes which were supported by self-prepared PES hollow fiber UF membranes were prepared for the pervaporation (PV) separation of ethanol from water. Impacts of PES support layer on the PV performances of PDMS/PES composite membranes were studied. Experimental results showed that, while working as a support to PDMS active layer, PES hollow fiber membrane could affect the PV performance of PDMS/PES membranes greatly. Pervaporation performance of the membrane which its PES support layer had bigger porosity and bigger mean pore size was apparently superior to that of the membrane which its PES support layer had smaller porosity and smaller mean pore size. After being treated with ethanol and hexane, PES membrane was dried in air for 20 min before being immersed in PDMS coating solution; the prepared PDMS/PES membrane had the best PV performance with a permeate flux of 330 g/(m^2 h) and a separation factor of 5.8. Effects of process parameters, such as feed temperature, permeate pressure, and feed flow rate, on membrane properties were investigated. For the separation of a 5 wt.% ethanol–water mixture, with an increase in feed temperature from 30 to 60˚C, water flux and ethanol flux increased from 51 to 328 g/(m^2 h) and from 14 to 88 g/(m^2 h), respectively; the variation of permeation flux followed the Arrhenius relationship and the activation energy values for water and ethanol were 54.54 and 53.44 kJ/mol, respectively; separation factor varied from 5.1 to 6.0. When the feed temperature was 50˚C and feed concentration was 5 wt.%, with an increase in permeate-side pressure from 1 to 40 mm Hg, water flux dropped sharply from 334 to 14 g/(m^2 h) and ethanol flux dropped moderately from 82 to 22 g/(m^2 h), and as a result, separation factor increased. With the increase in feed flow rate from 0.1 to 10 L/min, both flux and separation factor increased rapidly at first and then leveled off at 2 L/min for the reason of concentration polarization.

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Keywords: Polydimethylsiloxane (PDMS); Polyethersulfone (PES); Hollow fiber membrane; Pervaporation; Ethanol–water

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1. Introduction

Organophilic pervaporation separation of ethanol from water has been studied widely for its potential applications in the areas of the food and beverage industry, biochemical engineering, and environmental engineering. Since the concentration of ethanol in fermentation broth is usually in the order of a few percent by weight, pervaporation process could be integrated into an alcohol fermentation process so as to achieve the continuous production, and it has been shown to be effective for the improvement of fermentation production [1–9]. For this reason, separating ethanol from water by pervaporation has been widely investigated. For most of the studies, rubber polymers, such as poly (dimethylsiloxane) (PDMS) [1,3,10], poly (acetylene) polymers [11,12], carbon molecular sieve [7], and hydrophobic zeolite [8], have been used as membrane materials. Among these polymers, PDMS has several advantages, such as low polarity, high flexibility, and low polymerization temperature, and is being used as a membrane material. In addition, with two symmetrical hydrophobic methyl groups in each repeating unit, PDMS has been found to have a high selectivity towards ethanol [13]. The solubility parameters for PDMS [14], ethanol, and water [15] are 15.5, 26, and 47.9 $\text{MPa}^{2/1}$, respectively. In fact, PDMS is a notable hydrophobic material that discourages the transportation of water molecules, while at the same time, allows the transportation of a wide range of larger organic molecules. For this reason, pervaporation removal of ethanol from aqueous solution by PDMS membrane is of great interest for researchers.

For the pervaporation separation of ethanol, most of the studies have been concentrated on the flat sheet composite membrane [1,2,4,5], although hollow fiber composite membrane has much higher packing density and larger membrane area than flat sheet membrane [16–18]. From an application point of view, hollow fiber membrane seems to be a better alternative than flat sheet membrane. For the preparation of hollow fiber composite membrane, the selection of the support layer material is very important [2,19]. The impact of the support layer on the membrane performance depends on the morphology and chemical nature of the support membrane. The polymers which are used to prepare the hollow fiber support layer are mainly polysulfone, polyethersulfone (PES), polyetherimide, polyimide, polyacrylonitrile, and polyester. Generally, PES is widely used for its good physical, chemical, and mechanical properties [20–22].

In this study, PES ultrafiltration (UF) hollow fiber membranes which had different cross-section structures were prepared by the dry/wet-spinning method. Then PDMS/PES composite hollow fiber membranes which had the same PDMS coating layer and different PES support layer were prepared by dip-coating method. Using the PDMS/PES membranes for the pervaporation of dilute ethanol aqueous, the effects of the preparing condition and the pretreating method of the PES membrane, as well as the operating conditions on pervaporation performance were discussed.

2. Experimental

2.1. Materials

Membrane support layer material, powder form PES (Mw 146×10^3), was obtained from Jida High Performance Material Co. Ltd (P.R. China). PDMS (Silicone Rubber 107, Mw 5000), cross-linking agent ethyl silicate, and curing agent dibutyltin dilaurate were purchased from Shanghai resin Company (P.R. China). Reagent grade N-methyyl-2-pyrrolidone (NMP), ethanol, and glycerol were used as non-solvent additives and were products of Shanghai Ruen Jie chemical reagent Company (P.R. China). Reagent grade ethanol and *n*-hexane were used for the pretreatment of PES hollow fiber support membrane and were obtained from Shanghai Ruen Jie chemical reagent Company (P.R. China).

2.2. Preparation of PES dope solution

PES dope solution was prepared by the following procedure. First, PES polymer was dried in an oven for 24 h at 80°C under vacuum to remove its moisture. Then, the non-solvent additive glycerol or ethanol was mixed with NMP in a glass bottle. After that, the dried polymer was added into the bottle to make the dope solution. Finally, the solution was heated in an oven at 60°C until it became homogeneous.

2.3. Spinning of PES hollow fiber support membrane

PES UF hollow fiber base membranes (PES1–PES4) were spun at 20°C employing the dry/wet-spinning method, described elsewhere [17]. Outer diameter and thickness of the hollow fibers were measured by an

Table 1
Composition of dope solution and bore fluid solution

Dope solution No.	Polymer concentration (%)	Polymer/additives/NMP ratio	Bore fluid solution
1	18	PES/Glycerol/NMP 18:4:78	NMP/H_2O 8:2
2	30	PES/Glycerol/NMP 30:5:65	NMP/H_2O 8:2
3	18	PES/Ethanol/NMP 18:15:67	NMP/H_2O 9:1
4	25	PES/Ethanol/NMP 25:10:65	NMP/H_2O 9:1

Table 2
Spinning parameter and dimension of PES hollow fiber membranes

Base Membrane No.	PES1	PES2	PES3	PES4
Dope solution No.	1	2	3	4
Dope fluid rate (mL/min)	1.0	0.4	1.2	0.7
Spinning temperature (℃)	20	20	20	20
External coagulant	Water	Water	Water	Water
Dope pressure (MPa)	0.12	0.6	0.1	0.25
Air gap distance (cm)	0	0	0	0
Coagulant bath temperature (℃)	20	20	20	20
Membrane outer diameter (μm)	1,180	1,000	990	1,010
Membrane inner diameter (μm)	640	770	650	570
Membrane thickness (μm)	270	115	170	220

optical microscope. Table 1 summarized the composition of the dope solutions and bore fluids. Spinning condition and the dimension of PES hollow fiber membranes were demonstrated in Table 2.

2.4. Pretreatment of PES hollow fiber membranes

After PES hollow fibers had been fabricated, they were first soaked in water for 3 d, then were pretreated by the use of the following ethanol–hexane–air solvent exchange drying procedure. First, taken out from water, the PES hollow fibers were immersed in pure ethanol for 1 h and then were taken out, repeated this process two more times with two new pure ethanol exchanges. Second, the ethanol-treated membranes were treated with pure *n*-hexane with the same three times immerse procedure as with the ethanol. After that, the membranes were dried naturally in ambient air for a certain period of time.

2.5. Preparation of PDMS/PES hollow fiber composite membranes

PDMS casting solution was prepared by dissolving PDMS, cross-linker (ethyl silicate), and curing agent (dibutyltin dilaurate) in an *n*-hexane solution, with the ratio of 10:1:0.5 (in weight). Immediately after the coating solution was prepared, PES hollow fiber UF membranes were put into the solution, after being immersed in the solution for 15 s, the coated membranes were dried in a sterile room at room temperature for 24 h. Repeat the procedure certain times, the cross-linked PDMS/PES hollow fiber composite membranes were prepared. For simplicity, PDMS/PES hollow fiber composite membranes were designated as M1, M2, M3, and M4 which used PES1, PES2, PES3, and PES4 as support layer in order.

2.6. Membrane UF performance

The UF property of PES membranes was studied by the measurement of pure water permeation flux (*J*) which was carried out by a self-made filtration device showed in Fig. 1. In our experiment, for each membrane, three samples were tested to obtain an average value. To get a steady flux, permeate was collected after the system run for at least 1 h at 0.1 MPa. Pure

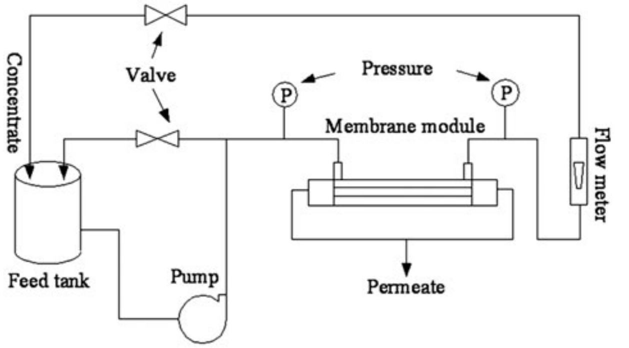

Fig. 1. Schematic diagram of UF experimental equipment.

water flux was measured at 25℃ and 0.1 MPa and was calculated by:

$$J_{\mathrm{U}} = V/(A \times T) \quad (1)$$

where J_{U} was membrane flux (L/m^2 h), V was permeation volume (L), A was effective membrane area, and T was microfiltration time (h).

2.7. Membrane characterization

In order to investigate the impacts of PES base membrane on PV properties of the PDMS/PES membranes, surface and cross-sectional morphologies of PES and PDMS/PES membranes were observed with scanning electron microscope apparatus (SEM) (JEOL Model JSM-6360 LV, Japan). First, membrane samples were fractured in liquid nitrogen to prevent the deformation of the samples. Second, coating the membranes with gold for 5 min under vacuum using the JS-1600 Ion Sputtering device was done. And then, the structures of the top surface, bottom surface, and cross-section were observed at 15 KV by the SEM.

Membrane porosity (ε) was determined by dry–wet weight method. The soaking liquid used for porosity measurement named Profil was supplied by IB-FT GmbH Germany. The porosity ε was calculated from the following equation:

$$\varepsilon = (w_1 - w_2)/\, A\delta_{\mathrm{m}}\rho \quad (2)$$

where w_1 is the weight of wet membrane (g), w_2 is the weight of dry membrane (g), A is the area of wet membrane, δ_{m} is the thickness of wet membrane (cm), and ρ is Profil density (1.87 g/cm^3). In our experiments, for each membrane, three samples were tested to obtain an average value.

The mean pore size (r_{m}) was defined by the filtration velocity method. The mean pore size was described by the Guerout–Elford–Ferry equation [23]

$$r_{\mathrm{m}} = \sqrt{(2.9 - 1.75\varepsilon) \times 8\eta l Q/(\varepsilon A \Delta P)} \quad (3)$$

where $\eta = 8.9 \times 10^{-4}$ Pa s (viscosity of pure water at 278 K), Q is permeation rate of pure water (m^3/s), l is the thickness of the membranes (mm), and ΔP is the operation pressure (0.1 MPa).

2.8. Pervaporation

Fig. 2 shows the schematic diagram of pervaporation apparatus used in this case. The hollow fiber membrane cell consisted three bundles of membranes and each bundle consisting six fibers. The length of the fibers was 20 cm and the ends of the hollow fiber bundles were glued with thermo epoxy resin. The characteristics of the hollow fiber membrane cell used in our experiments are given in Table 3. Before pervaporation experiment, hollow fiber membrane models were tested under 1.5 MPa to ensure there was no leakage. Dilute ethanol/water solution was used as the feed and was circulated by a circulation pump. The hollow fiber membrane cell was kept in a water bath and the temperature of the water bath was kept constant with a built-in booster heater controlled by a temperature controller. The pressure at permeate side was maintained at a vacuum of 10–40 mm Hg by a vacuum pump. After operation reached a steady state (about 1 h after the operation), collecting the permeate vapor in a liquid nitrogen cold trap was started. Permeate was then weighed and its composition was measured by gas chromatography with a thermal conductivity detector (TCD, Techcomp Ltd, GC7890). Permeation flux (J_{P}) and separation factor (α) are defined as:

$$J_{\mathrm{P}} = m/(\Delta t \times A) \quad (4)$$

$$\alpha = \left(y_{\mathrm{alcohol}}/y_{\mathrm{water}}\right)/\left(x_{\mathrm{alcohol}}/x_{\mathrm{water}}\right) \quad (5)$$

where m was the total amount of permeate collected during the time interval Δt, A was effective membrane area, x and y represented the mole fraction of a component in permeate and in feed, respectively.

3. Results and discussion

3.1. Characterizations of PES hollow fibers

In order to investigate the effects of PES base membrane on PV performance of PDMS/PES composite membrane, PES UF hollow fiber membranes (PES1–PES4) were fabricated. The cross-section morphologies of PES1–PES4 were presented in Fig. 3. Different membrane morphologies of PES1–PES4 were obtained under different membrane formation conditions as shown in Table 1. PES1 showed an asymmetric finger-like structure and had the outer and inner double skin layers; PES2 showed a sponge-like structure with a single skin layer; PES3 and PES4 had a finger-like structure with a single skin layer. PES1–PES4 had different porosities and different mean pore sizes as showed in Table 4. PES3 had the largest porosity and the biggest mean pore size, whereas PES2 demonstrated the smallest in porosity and mean pore size.

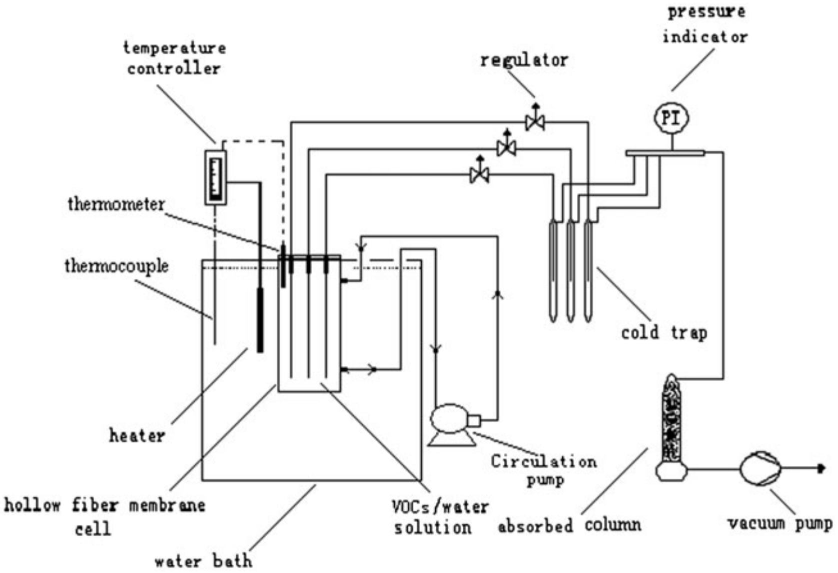

Fig. 2. Schematic diagram of pervaporation apparatus.

Table 3
Properties of hollow fiber membrane model

Housing material sealant	Stainless steel epoxy resin
Inside diameter of the cell (mm)	100
The height of the cell (mm)	350
The distance among bundles (mm)	52
Number of hollow fibers	18
Effective length of hollow fibers (mm)	200

PDMS/PES composite membrane (M3) which used PES3 as the support layer was prepared; the SEM characterizations of its surface and cross-section were carried out and were demonstrated in Fig. 4. The dense PDMS skin of about 7 μm was tightly adhered on the external surface of PES3, demonstrating a good compatibility of PDMS and PES. The internal surface of M3 was porous, while its external surface was smooth and glossy.

3.2. *Effect of hollow fiber base membrane on PV performance*

For the preparation of hollow fiber composite membranes, usually the support layer only acts as a mechanical support to the active layer and its resistance to PV flux is regarded as negligible. But sometimes, the support layer provides significant resistance to the flux and can affect separation factor significantly [2,18,19]. In an extreme case, however, transfer resistance of the support layer may become so dominant that the selectivity of the composite membrane even reaches the intrinsic selectivity of the support membrane. In Smart's experiment of separating toluene from toluene–water solution by silicone rubber membrane, a 40% reduction of toluene flux was found provided by the additional resistance of the hollow fiber support layer [18]. In Kim's experiment, toluene flux was increased by 41.4% after the pretreatment of the hollow fiber support membrane [2].

In this study, PDMS/PES hollow fiber composite membranes (M1–M4) which had the same PDMS coating layer and different support layer (PES1–PES4) were developed. The effects of support layer on pervaporation performance were studied using a 5 wt.% ethanol–water mixture at 10 mm Hg permeate pressure, 10 L/min feed flow rate, and different temperatures. PV performances from M1 to M4 were illustrated in Fig. 5. Total flux increased with the increase in feed temperature, the total flux of M3 was significantly larger than those of the others. Separation factor of M3 was also apparently bigger than those of the others. That is to say, using PES3 as the base membrane, M3 had the best PV performance. These results corresponded well with the measurement of pure water flux (Table 4) of the base membranes PES1–PES4.

From Table 4, we can see that the pure water fluxes of PES1–PES4 were significantly different from one another. The Pure water flux of PES2 was the smallest, only 1.20 L/(m^2 h), which meant that PES2 was not suitable to be used as a base membrane. Pure water flux of PES3 was 84.30 L/(m^2 h) which was the largest and was much larger than those of the others.

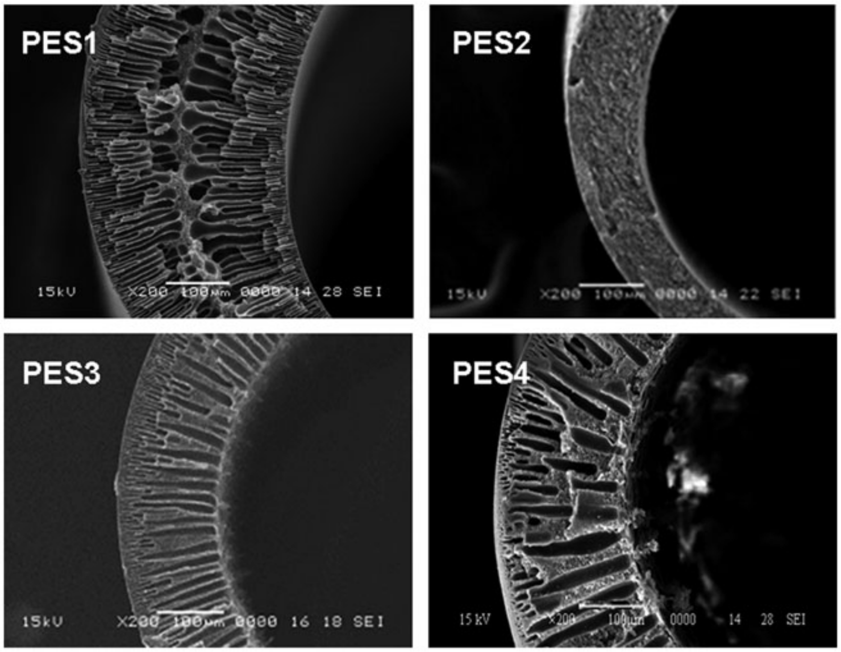

Fig. 3. Cross-section structure SEM of PES hollow fiber base membranes (PES1–PES4) (original magnification: 200×).

Table 4
Characterization and pure water permeation flux of different base membranes

Membrane	ε (%)	r_m (nm)	J (L/(m^2 h))
PES1	75.17	8	30.35
PES2	63.65	2	1.20
PES3	83.24	10	84.30
PES4	71.39	7	28.50

Pore structure of base membrane could have a big effect on pure water flux. For the PES UF membrane, the higher the porosity and the bigger the mean pore size are, the bigger the pure water flux will be. So, with high porosity and big mean pore size, PES3 had a very large pure water flux that its resistance to PV mass transfer could be regarded as negligible [2,18]. To decrease the resistance of base membrane, in the following experiments, PES3 was used as the base membrane.

3.3. *Effects of support layer pretreatment on PV performance*

For the preparation of hollow fiber composite membrane, usually, hollow fiber base membrane was used directly after the fabrication without pretreatment. However, according to the literatures [24,25], support layer pretreatment could have a notable impact on PV performance. To minimize the intrusion of PDMS into the support layer, in the making of PVDF support membrane, Vankelecom et al. used water-soluble polyethylene glycol as an additive to fill up the pores in the support layer [24]. According to Wang et al., they used alcohol to treat PVDF hollow fiber, and the N_2 permeation flux of the treated membrane increased by 3–4 times [25]. In this study, PES hollow fibers (PES3) were pretreated by the use of the so-called ethanol–hexane–air solvent exchange drying procedure as described in the Section 2.4. The effect of support layer pretreatment on PV performance was studied by a 5 wt.% ethanol–water mixture at 10 mm Hg, 10 L/min, and 50°C; the experimental results were illustrated in Table 5.

Base membrane pretreatment had a big effect on PV properties, when PES3 was pretreated with ethanol and hexane and was coated immediately after the treatment, the flux of the pretreated M3 was more than doubled compared with that of the non-treated M3. This is because after being treated with ethanol and hexane, the pores in the treated membrane were filled with ethanol molecules and hexane molecules as shown in Fig. 6, so when coated with PDMS polymer, PDMS molecules could not intrude into the pores of PES base membrane. Therefore, the PDMS coating layer was relatively thinner, and resulted in a high flux (484 g/(m^2 h)) and a small separation factor (4.0).

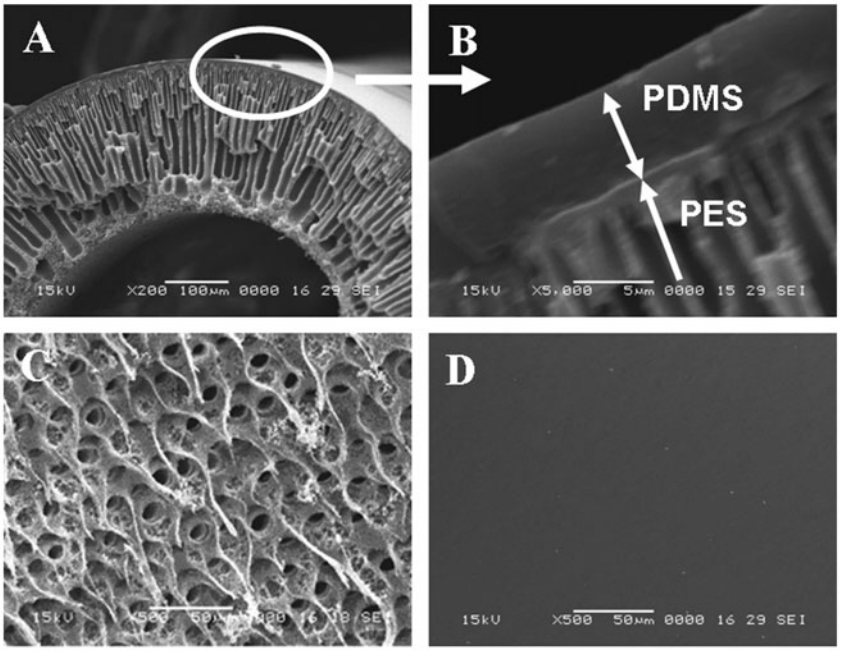

Fig. 4. SEM structures of PDMS/PES hollow fiber composite membrane. A—cross-section (original magnification: 200×); B—cross-section (original magnification: 5,000×); C—internal surface (original magnification: 500×); D—external surface (original magnification: 500×).

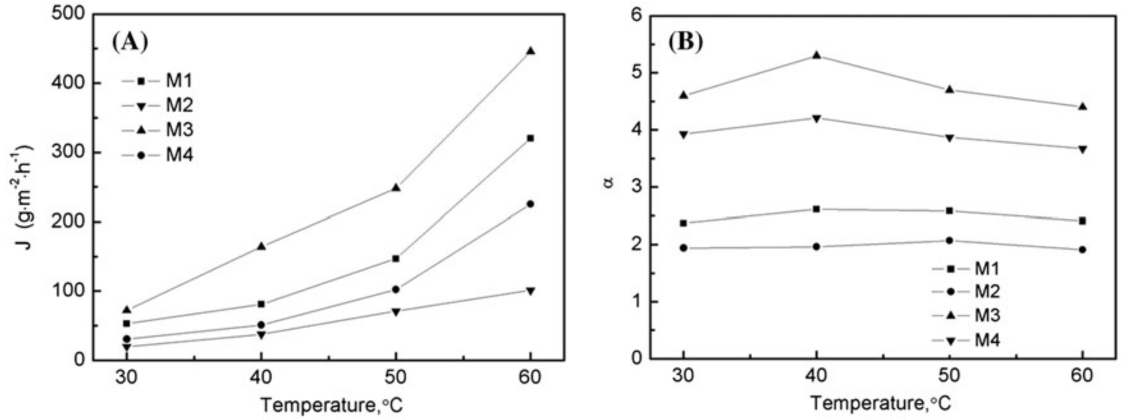

Fig. 5. Effect of support layers on permeation flux (A) and separation factor (B) (downstream pressure: 10 mm Hg; ethanol concentration in feed: 5 wt.%; feed flow rate: 10 L/min).

After treated with ethanol and hexane, some PES membranes were dried in air for 20 min before being immersed in PDMS coating solution. During the 20 min drying, the ethanol molecules and hexane molecules on the outer surface of the PES base membrane were evaporated. While the pores of PES base membrane were still filled with ethanol and hexane molecules. In fact, the ethanol and hexane molecules in the pores not only minimized the intrusion of PDMS in the support layer but also prevented the reduction of the porosity and the pore size [25]. On the other hand, the rapid evaporation of ethanol and hexane caused the outer surface of PES membrane to shrink, so the pore size on the outer surface of PES membrane was reduced [25], which was equal to the increase in thickness of the active layer. Because the resistance of PES support was still neglectable, the shrink of the membrane's outer surface had no effect

Table 5
Effects of the pretreatment of PES support membranes on pervaporation performances

Pretreatment ways	Flux ($g/(m^2\ h)$)	Separation factor
Without pretreatment	248	4.7
Immediately used after pretreatment	484	4.0
Put in the air for 20 min after pretreatment	330	5.8
Put in the air for 24 h after pretreatment	253	4.6

to the flux, but it caused the increase in separation factor. By conclusion, the ethanol and hexane molecules in PES pores and the shrink of the outer surface pore size led the PDMS/PES membrane to have the best PV performance with a permeate flux of 330 $g/(m^2\ h)$ and a higher separation factor of 5.8. But when the pretreated membranes were dried in air for 24 h before coated, the ethanol and hexane molecules both on the surface of the membrane and in the holes of the PES evaporated, the PV performance of the resulted membrane had no obvious difference with that of the untreated membrane. So in the following experiments, PES3 pretreated with ethanol–hexane and then dried in the air for 20 min was adopted for the preparation of PDMS/PES composite membrane.

3.4. Effects of feed temperature on membrane performance

For pervaporation, temperature is an important process parameter; it affects PV performance by varying vapor–liquid partitioning, altering sorption behavior of membrane, and changing diffusion coefficients of the components both in the feed and in the membrane. Temperature affects the diffusivity behavior and sorption behavior of the membrane in two ways [14], one by modifying the sorption–diffusion steps inside membrane, and the other by changing the activity driving force across the membrane. The higher the temperature is, the more intensive the thermal motions of the polymer molecules are and the larger the membrane free volume is.

Effect of feed temperature on total flux and separation factor as a function of feed concentration at 10 mm Hg and 10 L/min was shown in Fig. 7. With the increase in feed temperature, total flux increased significantly, but separation factors only varied a little, and it increased slightly to a maximum, then decreased. For the 5 wt.% solution, separation factor was in a range of 5.1–6.0 and the maximum separation factor was observed at 40°C. A similar result was observed by Nasiri and Aroujalian [26], who investigated the pervaporation separation of ethanol aqueous by the use of composite PDMS membrane supported by PVDF-PP. Nasiri and Aroujalian [26] concluded that the increase in total selectivity with temperature is for the reason of the increase in diffusion selectivity. But when temperature is too high, both sorption selectivity and diffusion selectivity decrease according to molecular dynamics simulation technique.

When ethanol concentration was 5 wt.%, with the increase in feed temperature from 30 to 60°C, total flux increased apparently from 66 to 483 $g/(m^2\ h)$, water and ethanol fluxes increased from 51 to 328 $g/(m^2\ h)$ and from 14 to 88 $g/(m^2\ h)$, respectively, as shown in Fig. 8(A). According to solution–diffusion mechanism, Arrhenius-type function can be used to express the effect of temperature on flux as follows:

$$J = J_0 \exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

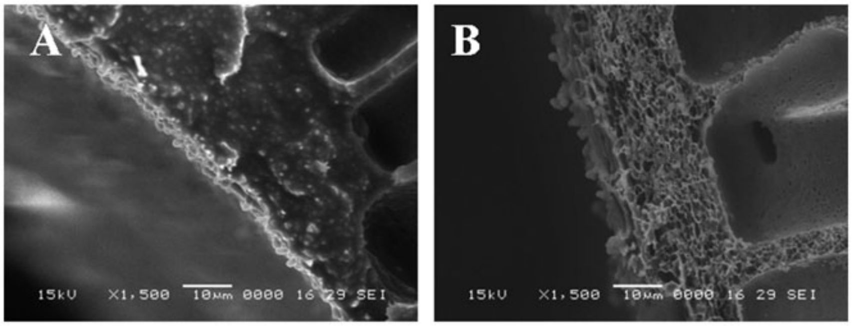

Fig. 6. SEM cross-sectional structures of PES3 hollow fiber membranes (original magnification: 1,500×). A—disposed with ethanol and hexane; B—without disposition with ethanol and hexane.

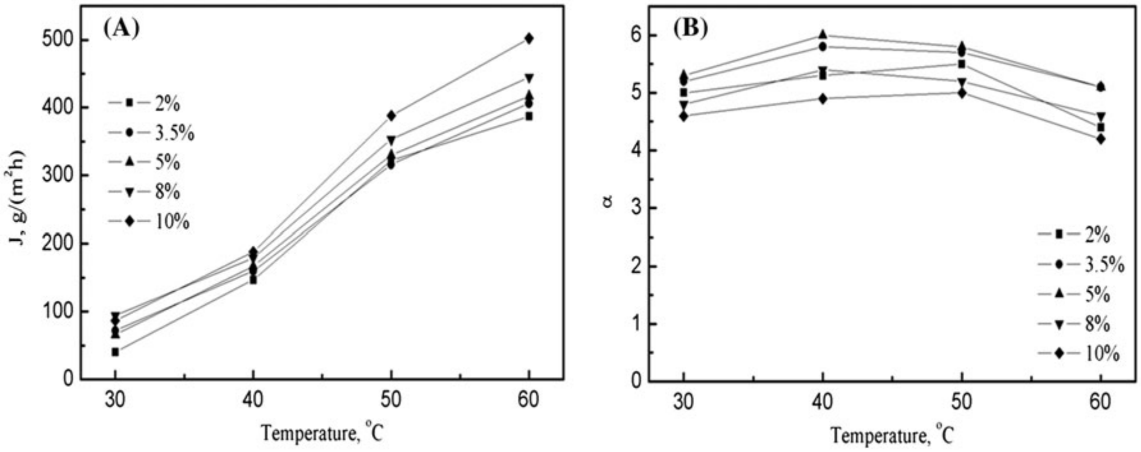

Fig. 7. Effect of feed temperature on total flux (A) and separation factor (B) as a function of feed concentration (downstream pressure: 10 mm Hg; feed flow rate: 10 L/min).

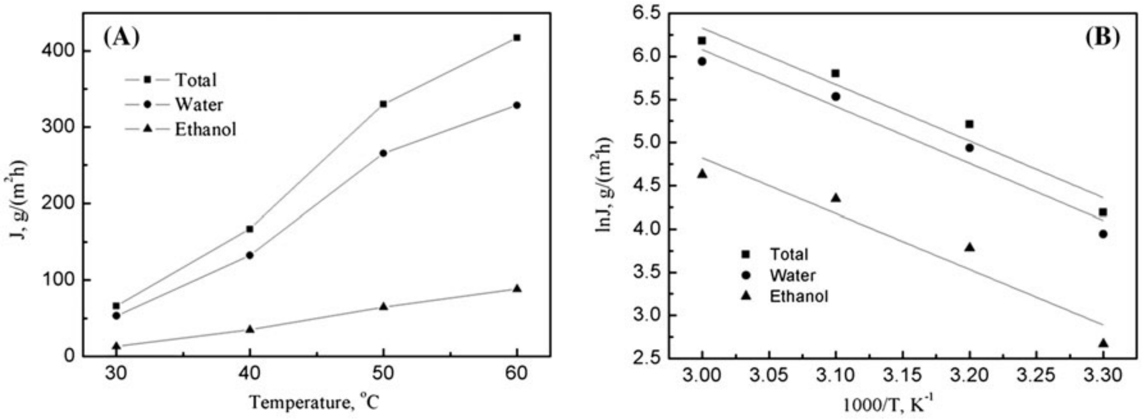

Fig. 8. Effect of feed temperature on pervaporation performance: (A) total flux, water flux, and ethanol flux; (B) the relation between ln(*J*) and $1/T$ (downstream pressure: 10 mm Hg; ethanol concentration in feed: 5 wt.%; feed flow rate: 10 L/min).

where J_0 is pre-exponential factor, J is permeate flux, E_a is permeation activation energy which represents the relative change of the flux to the change of temperature, R is gas constant, and T is absolute feed temperature. A higher value of E_a means a more sensitive behavior towards temperature alteration. In order to get the value of E_a of each component, a semi-logarithmic plot of permeation flux against reciprocal of absolute temperature ($1/T$) was developed, as showed in Fig. 8(B). The calculated values of E_a of total, water, and ethanol were 54.54, 54.79, and 53.44 kJ/mol, respectively. There was no significant difference in the E_a of total, water, and ethanol, and this also explained why with the increase in operating temperature, total flux increased and selectivity kept nearly constant (Fig. 6). These results were in agreement with the study of Yi et al. [27] who used vinyltriethoxysilane (VTES) modified silicalite-1/PDMS hybrid pervaporation membrane to separate ethanol aqueous. They found that E_a for water and ethanol were close and were in the range of 37.29–43.40 and 38.66–42.73 kJ/mol, respectively. In the investigation of the effect of PDMS molecular weights on the pervaporation performance of PDMS/ceramic composite membranes for the separation of ethanol from aqueous solutions, Wei et al. [28] got similar results that the values of E_a for total, water, and ethanol they calculated were 30.13–36.18, 29.53–35.84, and 33.93–37.22 kJ/mol, respectively.

3.5. Effect of permeate-side pressure on PV performance

The effects of permeate-side pressure on PV performances including total flux, water flux, ethanol flux, and separation factor were examined with a 5 wt.% ethanol–water mixture at 10 L/min. When the pressure in permeate side increases, mass transfer driving force decreases, so permeate flux decreases. As showed in Fig. 9, as pressure increased from 1 to 40 mm Hg, total flux dropped non-linearly. For the reason that the saturated vapor pressure of water is lower than that of the ethanol, permeate-side pressure has a significant effect on water flux but has only a modest effect on ethanol flux. So, we could find in Fig. 10, with the variation of permeate-side pressure from 1 to 40 mm Hg at 50℃, water flux decreased sharply from 334 to 14 g/(m^2 h), ethanol flux dropped moderately only from 82 to 22 g/(m^2 h).

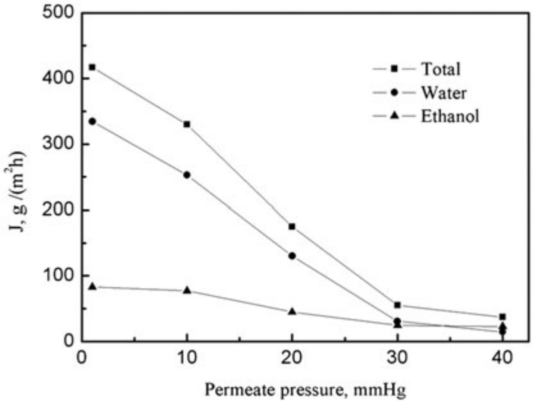

Fig. 10. Effect of downstream pressure on total flux, water flux, and ethanol flux (feed temperature: 50℃; ethanol concentration in feed: 5 wt.%; feed flow rate: 10 L/min).

The relationship between flux and permeate-side pressure can be expressed by the following equation in terms of partial pressure [29,30]:

$$J_i = J_{i0}(c_{i'}\gamma_{i'}p_{i0} - p_{i''}) \tag{7}$$

where J_i (cm^3/(cm^2 s)) is the permeation flux of species i, J_{i0} (cm^3/(cm^2 s mm Hg)) is the normalized permeation flux of species i, $c_{i'}$ is the mole fraction of species i on upstream surface of the membrane, p_{i0} (mm Hg) is the saturation vapor pressure of pure i at feed temperature, $\gamma_{i'}$ is the activity coefficient of i in feed, and $p_{i''}$ (mm Hg) is the partial pressure of i of the permeate-side of membrane. For the 5 wt.% ethanol–water solution (ethanol mole fraction 0.02), when feed temperature is 50℃, the activity coefficients of ethanol and water are 4.67 and 1.0, the saturation vapor pressures of pure ethanol and pure water are 222.0 and 92.9 mm Hg, respectively,. The relationship between permeate-side pressure and solute flux then can be expressed as follows:

$$J_{\text{Ethanol}} = J_{\text{Ethanol0}}(20.4 - p_{\text{Ethanol}''}) \tag{8}$$

$$J_{\text{Water}} = J_{\text{Water0}}(91.0 - p_{\text{Water}''}) \tag{9}$$

Apart from influencing driving force, Permeate-side pressure also has impact on the diffusion path of permeates. When permeate-side pressure decreases, pressure gradient in the membrane increases which makes the diffusion path shortened. On the other hand, with the increase in permeate-side pressure, liquid transfer path stretches into vapor transfer space, and liquid transportation becomes the domination of

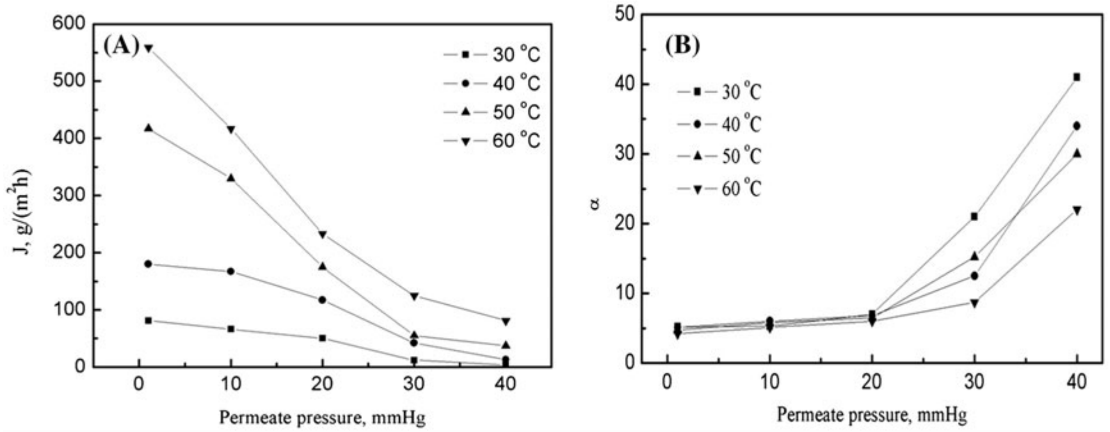

Fig. 9. Effect of downstream pressure on total flux (A) and separation factor (B) as a function of feed temperature (ethanol concentration in feed: 5 wt. %; feed flow rate: 10 L/min).

total mass transfer process and causes the decreasing of the total permeate rate. As it says [14]: "If permeate-side pressure is raised and approaches the vapor pressure of water, water transport may be reduced so significantly that convective flow practically ceases, stagnating the permeate."

The fact that, with an increase in permeate-side pressure, water flux decreased more dramatically than that of the ethanol caused an increase in separation factor as shown in Fig. 9(B). This suggests that, with the increase in the liquid transfer depth and the decrease in the vapor transfer depth, more ethanol can pass through the membrane. In other words, ethanol can more easily pass through the wet space inside the membrane than water can. This is because the solubility parameter of ethanol is close to that of the membrane [14,15]; therefore, ethanol molecules can be more easily solved by membrane than water molecules. As a result, selectivity may be determined by the liquid transfer depth and will be greater when permeate-side pressure approaches solution vapor pressure. In addition, Fig. 9(B) also shows that, when permeate-side pressure was below 20 mm Hg, its effect on selectivity was not obvious, but when permeate-side pressure was above 20 mm Hg, its effect on selectivity was significant. This information is useful for the determination of permeate-side pressure.

3.6. Effect of feed flow rate on PV performance

Effects of feed flow rate on PV performances including total flux, ethanol flux, water flux, and separation factor have been investigated using the PES3 hollow fiber membrane under experimental conditions of ethanol concentration 5 wt.%, feed temperature 60℃, and permeate-side pressure 10 mm Hg. As Fig. 11 demonstrated, with the increase in feed flow rate, total flux, ethanol flux, water flux, and separation factor, all increased rapidly at first and then leveled off at feed flow rate 2 L/min. These results were in accordance with the findings reported in the literature [31] which used a hybrid pervaporation–distillation separation process to recover ethanol from aqueous solution. When membranes with high selectivity and high permeability were used for the pervaporation of low concentration aqueous, concentration polarization may exist in the boundary layer adjacent to the membrane surface. The PDMS membrane has much higher permeability and selectivity for ethanol than for water, so we believe concentration polarization occurred in this study and it was confirmed by Fig. 11. When feed flow rate increased from 0.1 to 2 L/min, all the parameters of total flux, ethanol flux, water flux, and separation factor increased linearly. It means that concentration polarization was the control step of mass transfer when flow rate was less than 2 L/min. When feed flow rate was higher than 2 L/min, there was not an obvious increase for both flux and separation factor. So in this situation, membrane resistance became the control step of mass transfer. Consequently, to study membrane permeation properties for dilute solutions, feed flow rate must be big enough to eliminate the influence of concentration polarization.

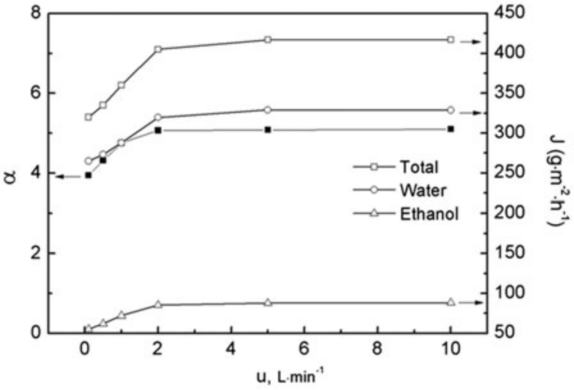

Fig. 11. Effects of feed flow rate on total flux, water flux, ethanol flux, and separation factor (downstream pressure: 10 mm Hg; feed temperature: 60℃; ethanol concentration in feed: 5 wt.%).

4. Conclusions

PES hollow fiber UF membranes with different pore structures were fabricated employing the dry/wet-spinning method. Using these PES hollow fiber UF membranes as support layer, PDMS/PES hollow fiber composite membranes which had the same PDMS coating layer were developed to exam the effect of support layer on pervaporation performances. The hollow fiber support layer was observed to have a significant effect on both total flux and ethanol selectivity. Pervaporation properties of the membrane with big porosity and big mean pore size were apparently superior to those of the membranes with small porosity and small mean pore size. When PES membranes were dried in air for 20 min after treated with ethanol and hexane and then were immersed in PDMS coating solution, the prepared PDMS/PES membranes had the best PV performances with a permeate flux of 330 g/(m^2 h) and a separation factor of 5.8.

Pervaporation properties of dilute ethanol aqueous through PDMS/PES membranes were investigated, the effects of process parameters such as temperature, permeate pressure, and feed flow rate were discussed.

With the increase in feed temperature from 30 to 60˚C, total flux increased significantly, but separation factors increased slightly to a maximum then decreased; for the 5 wt.% mixture, water and ethanol fluxes increased from 51 to 328 $g/(m^2 h)$ and from 14 to 88 $g/(m^2 h)$, selectivity varied from 5.1 to 6.0. When the permeate-side pressure was increased from 1 to 40 mm Hg, total flux showed a non-linear decrease, permeate-side pressure had little effect on selectivity while held below 20 mm Hg; however, when pressure was above 20 mm Hg, the effect was significant. With the increase in feed flow rate from 0.1 to 10 L/min, both flux and separation factor increased rapidly at first and then leveled off at feed flow rate 2 L/min for the reason of concentration polarization at boundary layer; when feed flow rate was less than 2 L/min, concentration polarization was the control step of mass transfer, but when feed flow rate was higher than 2 L/min, membrane resistance became the control step of mass transfer.

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References

[1] W. Van Hecke, P. Vandezande, S. Claes, S. Vangeel, H. Beckers, L. Diels, H. De Wever, Integrated bioprocess for long-term continuous cultivation of Clostridium acetobutylicum coupled to pervaporation with PDMS composite membranes, Bioresour. Technol. 111 (2012) 368–377.

[2] H.J. Kim, S.S. Nah, B.R. Min, A new technique for preparation of PDMS pervaporation membrane for VOC removal, Adv. Environ. Res. 6 (2002) 255–264.

[3] M. Keshavarz Moraveji, A. Raisi, S.M. Hosseini, E. Esmaeeli, G. Pazuki, CFD modeling of hydrophobic pervaporation process: Ethanol/water separation, Desalin. Water Treat. 51 (2013) 3445–3453.

[4] S.S. Gaykawad, L.A.M. van der Wielen, A.J.J. Straathof, Effects of yeast-originating polymeric compounds on ethanol pervaporation, Bioresour. Technol. 116 (2012) 9–14.

[5] C.Y. Chen, X.Y. Tang, Z.Y. Xiao, Y.H. Zhou, Y. Jiang, S.W. Fu, Ethanol fermentation kinetics in a continuous and closed-circulating fermentation system with a pervaporation membrane bioreactor, Bioresour. Technol. 114 (2012) 707–710.

[6] E.J. Jeon, A.S. Kim, Y.T. Lee, Pervaporation of butanol/water mixtures using siloxane polymer/ceramic composite membranes, Desalin. Water Treat. 48 (2012) 17–26.

[7] K.S. Liao, Y.J. Fu, C.C. Hu, J.T. Chen, D.W. Lin, K.R. Lee, K.L. Tung, Y.C. Jean, J.Y. Lai, Microstructure of carbon molecular sieve membranes and their application to separation of aqueous bioethanol, Carbon 50 (2012) 4220–4227.

[8] D. Jeong, J. Oh, I. Yum, Y. Lee, Removal of VOCs from their aqueous solution by pervaporation with PDMS-zeolite composite membrane, Desalin. Water Treat. 17 (2010) 242–247.

[9] G.P. Liu, W. Wei, H. Wu, X.L. Dong, M. Jiang, W.Q. Jin, Pervaporation performance of PDMS/ceramic composite membrane in acetone butanol ethanol (ABE) fermentation–PV coupled process, J. Membr. Sci. 373 (2011) 121–129.

[10] F. Qin, S.F. Li, P.Y. Qin, M. Karim, T.W. Tan, A PDMS membrane with high pervaporation performance for the separation of furfural and its potential in industrial application, Green Chem. 16 (2014) 1262–1273.

[11] A.G. Fadeev, S.S. Kelley, J.D. McMillan, Y.A. Selinskaya, V.S. Khotimsky, V.V. Volkov, Effect of yeast fermentation by-products on poly[1-(trimethylsilyl)-1-propyne] pervaporative performance, J. Membr. Sci. 214 (2003) 229–238.

[12] J.A. González-Marcos, C. López-Dehesa, J.R. González-Velasco, Effect of operation conditions in the pervaporation of ethanol–water mixtures with poly(1-trimethylsilyl-1-propyne) membranes, J. Appl. Polym. Sci. 94 (2004) 1395–1403.

[13] S.F. Li, F. Qin, P.Y. Qin, M. Karim, T.W. Tan, Preparation of PDMS membrane using water as solvent for pervaporation separation of butanol–water mixture, Green Chem. 15 (2013) 2180–2190.

[14] M. Peng, L.M. Vane, S.X. Liu, Recent advances in VOCs removal from water by pervaporation, J. Hazard. Mater. 98 (2003) 69–90.

[15] H.l. Zhou, Y. Su, X.R. Chen, Y.H. Wan, Separation of acetone, butanol and ethanol (ABE) from dilute aqueous solutions by silicalite-1/PDMS hybrid pervaporation membranes, Sep. Purif. Technol. 79 (2011) 375–384.

[16] D. Wang, K. Li, W.K. Teo, Porous PVDF asymmetric hollow fiber membranes prepared with the use of small molecular additives, J. Membr. Sci. 178 (2000) 13–23.

[17] Y.M. Wei, Z.L. Xu, F.A. Qusay, K. Wu, Polyvinyl alcohol/polysulfone (PVA/PSF) hollow fiber composite membranes for pervaporation separation of ethanol/water solution, J. Appl. Polym. Sci. 98 (2005) 247–254.

[18] J. Smart, R.C. Schucker, D.R. Lloyd, Pervaporative extraction of volatile organic compounds from aqueous systems with use of a tubular transverse flow module, J. Membr. Sci. 143 (1998) 137–157.

[19] F.T. de Bruijn, L. Sun, Ž. Olujić, P.J. Jansens, F. Kapteijn, Influence of the support layer on the flux limitation in pervaporation, J. Membr. Sci. 223 (2003) 141–156.

[20] C.S. Zhao, J.M. Xue, F. Ran, S.D. Sun, Modification of polyethersulfone membranes—A review of methods, Prog. Mater. Sci. 58 (2013) 76–150.

[21] J.C. Dang, Y.T. Zhang, Z. Du, H.Q. Zhang, J.D. Liu, Antibacterial properties of PES/$CuCl_2$ three-bore hollow fiber UF membrane, Water Sci. Technol. 66 (2012) 799–803.

[22] Y. Chen, J. Dang, Y. Zhang, H. Zhang, J. Liu, Preparation and antibacterial property of PES/$AgNO_3$ three-bore hollow fiber ultrafiltration membranes, Water Sci. Technol. 67 (2013) 1519–1524.

[23] C.S. Feng, B.L. Shi, G.M. Li, Y.L. Wu, Preparation and properties of microporous membrane from poly (vinylidene fluoride-co-tetrafluoroethylene) (F2.4) for membrane distillation, J. Membr. Sci. 237 (2004) 15–24.

[24] I.F.J. Vankelecom, B. Moermans, G. Verschueren, P.A. Jacobs, Intrusion of PDMS top layers in porous supports, J. Membr. Sci. 158 (1999) 289–297.

[25] D.L. Wang, K. Li, W.K. Teo, Porous PVDF asymmetric hollow fiber membranes prepared with the use of small molecular additives, J. Membr. Sci. 178 (2000) 13–23.

[26] H. Nasiri, A. Aroujalian, A novel model based on cluster formation for pervaporation separation of polar components from aqueous solutions, Sep. Purif. Technol. 72 (2010) 13–21.

[27] S.L. Yi, Y. Su, Y.H. Wan, Preparation and characterization of vinyltriethoxysilane (VTES) modified silicalite-1/PDMS hybrid pervaporation membrane and its application in ethanol separation from dilute aqueous solution, J. Membr. Sci. 360 (2010) 341–351.

[28] W. Wei, S.S. Xia, G.P. Liu, X.L. Dong, W.Q. Jin, N.P. Xu, Effects of polydimethylsiloxane (PDMS) molecular weight on performance of PDMS/ceramic composite membranes, J. Membr. Sci. 375 (2011) 334–344.

[29] W.C. Ji, S.K. Sikdar, S.T. Hwang, Modeling of multicomponent pervaporation for removal of volatile organic compounds from water, J. Membr. Sci. 93 (1994) 1–19.

[30] J.G. Wijmans, R.W. Baker, A simple predictive treatment of the permeation process in pervaporation, J. Membr. Sci. 79 (1993) 101–113.

[31] J.B. Haelssig, A.Y. Tremblay, J. Thibault, X.M. Huang, Membrane dephlegmation: A hybrid membrane separation process for efficient ethanol recovery, J. Membr. Sci. 381 (2011) 226–236.