Preparation of PFSA-PVA/PSf Hollow Fiber Membrane for IPA/H₂O Pervaporation Process

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ABSTRACT: Using Na^+ form of perfluorosulfonic acid (PFSA) and poly(vinyl alcohol) (PVA) as coating materials, polysulfone (PSf) hollow fiber ultrafiltration membrane as a substrate membrane, PFSA-PVA/PSf hollow fiber composite membrane was fabricated by dip-coating method. The membranes were post-treated by two methods of heat treatment and by both heat treatment and chemical crosslinking. Maleic anhydride (MAC) aqueous solution was used as chemical crosslinking agent using 0.5 wt % H_2SO_4 as a catalyst. PFSA-PVA/PSf hollow fiber composite membranes were used for the pervaporation (PV) separation of isopropanol (IPA)/H_2O mixture. Based on the experimental results, PFSA-PVA/PSf hollow fiber composite membrane is suitable for the PV dehydration of IPA/H_2O solution. With the increment of heat treatment temperature, the separation factor increased and the total permeation flux decreased. The addition of PVA in PFSA-PVA coating solution was favorable for the improvement of the separation factor of the composite membranes post-treated by heat treatment. Compared with the membranes by heat treatment, the separation factors of the composite membranes post-treated by both heat treatment and chemical crosslinking were evidently improved and reached to be about 520 for 95/5 IPA/water. The membranes post-treated by heat had some cracks which disappeared after chemical crosslinking for a proper time. Effects of feed temperature on PV performance had some differences for the membranes with different composition of coating layer. The composite membranes with the higher mass fraction of PVA in PFSA-PVA coating solution were more sensitive to temperature. It was concluded that the proper preparation conditions for the composite membranes were as follows: firstly, heated at 160°C for 1 h, then chemical crosslinking at 40°C for 3 h in 4% MAC aqueous solution. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 370–379, 2008

Key words: pervaporation; hollow fiber membrane; perfluorosulfonic acid; poly(vinyl alcohol) (PVA); isopropanol (IPA)/water mixture

INTRODUCTION

Pervaporation (PV) is a relatively new membrane process suitable for separating liquid mixtures, especially for the azeotrope and temperature-sensitive products.[1–3] The dehydration of isopropanol (IPA) aqueous solution by PV process was studied.[4,5] Selecting one or more proper polymers and preparing a membrane with high performances are the key factors for PV process. Perfluorosulfonic acid (PFSA) (represented by Dupont's product Nafion) is a perfluoro-polymer consisting of a polytetrafluoroethylene (PTFE) backbone and regular spaced long perfluorovinyl ether pendant side chains terminated by a sulfonate ionic. Its chemical structure is:
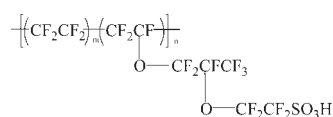
where H^+ can be exchanged by Na^+ or other cations. It has excellent chemical, thermal stability, and mechanical property.[6] PFSA has been used for PV process of many liquid mixtures. For example, the dehydration of nitric acid,[7] acetic acid,[8,9] and iodic acid[10] aqueous solution and the separation process for organic/organic system[11,12] have been investigated in recent years. PFSA polymer membrane also was used in the dehydration process for IPA/H_2O system,[13,14] but its separation factor appeared to be low. On the other side, poly(vinyl alcohol) (PVA) as a favorable membrane material shows a better separation factor for alcohol/H_2O PV process, but its permeation flux appears to be low.[15,16] Hollow fiber membrane with many advantages compared with flat membrane has been used for PV field.[17–21] However, there are a few attempts to prepare hollow fiber composite membranes by dip-coating, interfacial polymerization, and grafting methods.[15,22,23] Shao et al.[24] reported the Nafion/PVA composite membrane for direct methanol fuel cell. The addition of PVA in PFSA solution reduced the crossover of methanol and the selectivity revealed the best point at the weight ratio of 1 : 1 PVA : Nafion. In this article,

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PFSA and PVA were used for the fabrication of PFSA-PVA/polysulfone (PSf) hollow fiber composite membrane with PSf ultrafiltration (UF) membrane (self-prepared) as a substrate by dip-coating method. Three hollow fiber UF membranes were firstly considered as candidates for the porous substrate, i.e., PVDF, PAN, and PSf hollow fiber UF membranes. The shrinkage of pore structure of PVDF and PAN UF membranes were found during annealing process. Thus, PSf UF membrane was selected as the substrate support because of its better thermal resistance and excellent mechanical properties. IPA/H$_2$O mixture was used to examine the PV performance of the prepared composite membranes.

EXPERIMENTAL

Materials

PFSA in Na$^+$ form (PFSA-Na) in granular form was recovered from a deteriorated ion exchange membrane F-8020 (ASAHI Glass Company, Japan) used in chlor-alkali industry. F-8020 membrane is PFSA/perfluorocarboxylic acid composite flat membrane reinforced by PTFE fibers. The recovery procedure is described as follows: Firstly, a deteriorated F-8020 membrane was regenerated with 8% hydrochloride solution at 80°C for 2 h to remove the fouling of F-8020 membrane. Secondly, a dissolution process was carried out by putting the regenerated membrane into an autoclave with a certain amount of water and IPA (1 : 1 ratio).[25–27] The PFSA resin in F-8020 membrane was dissolved at high temperature. Finally, the solution was cooled to room temperature and filtrated to obtain clear liquid. PFSA powder was obtained after evaporating.

PSf in powder form was obtained from Shuguang Chemical Co. (China) and used as UF membrane material. PVA (1750 ± 50), maleic anhydride (MAC), and N,N-dimethylacetamide (DMAC) were purchased from Shanghai Chemical Agent Co. (China). IPA in reagent grade was obtained from Shanghai Heiwei Shisi Agent Co. (China).

Preparation of PSf UF membranes and PFSA-PVA/PSf hollow fiber composite membranes

PSf UF membrane as a substrate membrane was spun by dry/wet method, as described elsewhere.[28,29] The composition of the dope solution was PSf/PVP/DMAc 20/5/75 and deionized water was used as inner and external coagulation liquid. The spinneret has an outer and inner diameter of 900 and 600 μm, respectively. The ratio of dope flow rate to bore fluid rate was constant in the spinning process. The nascent fiber was not drawn (no extension). That is to say the flow rate for spinning was

nearly equal to the falling rate in the coagulation bath. The prepared fibers were immersed in the deionized water for above 24 h to eliminate the residual solvent in the membrane. Then, the fibers were immersed in IPA for 2 h and dried in air to alleviate the shrinkage of void structure before coating.

PFSA-PVA coating solution with a desired concentration and composition was prepared by dissolving PFSA and PVA in water at 90°C by agitation. Then, PFSA-PVA/PSf hollow fiber composite membranes were fabricated by immersing PSf UF membranes in the PFSA-PVA coating solution for 30 s. The coated membranes were then hung and dried overnight at room temperature in air. Each fiber was dip-coated and dried twice by the same way. The coated fibers were post-treated by heat treatment or by both heat treatment and chemical crosslinking. The heat treatment method is that the coated fibers were heat treated for 1 h at 120–160°C in the vacuum drying oven. The mixed solution of 4% MAC and 0.5% H$_2$SO$_4$ was used as the crosslinking agent. The composite membranes could be chemically crosslinked by immersing the coated membranes in the crosslinking agent solution for a certain time and then dried again in air. The detailed preparation conditions of each membrane were listed in Tables I and II.

PV separation of IPA/H$_2$O solution

The schematic diagram of PV apparatus is shown in Figure 1. To measure the separation performances of the composite membranes, six fibers with 14 cm length were bundled into one membrane module. Two ends of the module were glued with thermoset epoxy resin. Each sample membrane was tested with three modules at the same time. A full tank of IPA/H$_2$O as feed solution and the membrane modules were wholly placed in a thermostatic bath. The feed composition for all PV processes was 95% IPA/H$_2$O in this study. The permeate side was kept below 0.1 kPa. The permeate was collected with cold trap cooled by liquid nitrogen. The variation of feed composition was neglected at one PV interval. The composition of permeate and feed liquid was measured by a gas chromatograph (Chromatography GC7890T, China). The PV separation factor is defined as:

TABLE I
The Preparation Conditions of PFSA-PVA/PSf Hollow Fiber Composite Membranes by Heat Treatment Method

Membrane no.	PFSA-Na : PVA	Heat treatment temperature (°C)
M11–M14	1 : 7	120, 140, 150, and 160
M21–M24	2 : 6	120, 140, 150, and 160
M31–M34	4 : 4	120, 140, 150, and 160
M41–M44	5 : 3	120, 140, 150, and 160
M51–M54	7 : 1	120, 140, 150, and 160

TABLE II
The Preparation Conditions of PFSA-PVA/PSf Hollow Fiber Composite Membranes by Both Heat Treatment and Chemical Crosslinking Method

Membrane no.	PFSA-Na : PVA	Heat treatment temperature (°C)	Chemical crosslinking	
			Time (h)	Temperature (°C)
M14-1	1 : 7	160	2	40
M24-1	2 : 6	160	2	40
M34-1	4 : 4	160	2	40
M44-1	5 : 3	160	2	40
M54-1	7 : 1	160	2	40
M44-2	5 : 3	160	2	30
M44-3	5 : 3	160	2	50
M44-4	5 : 3	160	1	40
M44-5	5 : 3	160	3	40
M44-6	5 : 3	160	5	40

$$\alpha = \frac{X_{H_2O}^{P}/X_{IPA}^{P}}{X_{H_2O}^{F}/X_{IPA}^{F}} \qquad (1)$$

where $X_{H_2O}^{P}$ and X_{IPA}^{P} are the weight fractions of H_2O, IPA of permeate, respectively, and $X_{H_2O}^{F}$ and X_{IPA}^{F} are the weight fractions H_2O, IPA of feed liquid, respectively.

The permeation flux is obtained as follows:

$$J = \frac{W}{A \times t} \qquad (2)$$

where W is total weight of the whole permeate over time t, A is the effective membrane area of one module, and t is the running time. The effective membrane area of hollow fibers is calculated upon the outer diameter of the fibers. It can be expressed as:

$$A = N \pi d_o l \qquad (3)$$

where A is the effective area of a membrane module, d_o is the outer diameter, l is the effective length of the fibers, and the N is the number of the fibers in one module.

Another parameter to be used to characterize the separation performance of composite membranes is
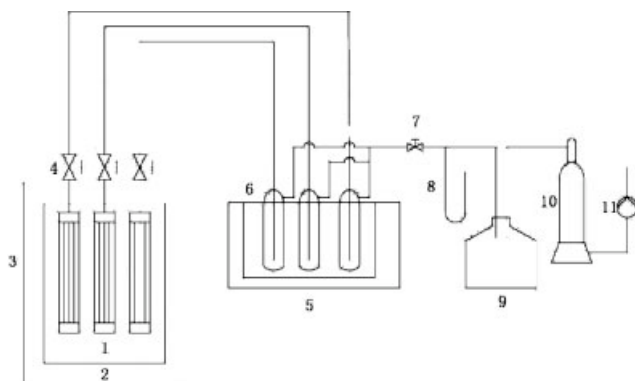

Figure 1 Schematic diagram of pervaporation apparatus.

TABLE III
Effects of Mass Fractions of PFSA in PFSA-PVA Coating Solution on PV Performance of PFSA-PVA/PSf Hollow Fiber Composite Membranes by Heat Treatment Method

Membrane no.	α	J (L m^{-2} h^{-1})	PSI (L m^{-2} h^{-1})	δ (μm)
M14	389	108	42,030	8.0
M24	253	181	45,940	2.0
M34	233	193	44,920	4.0
M44	226	156	39,800	9.0
M54	175	255	44,520	2.5

PV conditions: 95% IPA; temperature 50°C.

permeation separation index (PSI). It can be defined as:

$$PSI = \alpha \times J \qquad (4)$$

where α and J are the separation factor and the total permeation flux, respectively.

Morphology of the PFSA-PVA/PSf hollow fiber composite membranes

Membrane morphology was examined by a scanning electron microscope (SEM) (JEOL Model JSM-6360 LV, Japan). The inner surfaces, outer surfaces, and the cross sections of PFSA-PVA/PSf hollow fiber composite membranes were obtained by breaking the membranes in liquid nitrogen to avoid destroying the membrane structure of fibers. Top layer thicknesses of the membranes were estimated from SEM pictures and listed in Tables III and IV.

RESULTS AND DISCUSSION

PFSA-PVA/PSf hollow fiber composite membranes post-treated by heat treatment

Effect of heat treatment temperature on PV performance

The composite membranes with different coating layers from M11–M14 to M51–M54 were the fibers post-treated by heat treatment at different temperatures. Figure 2 shows that PV performances of the

TABLE IV
Effects of Mass Fractions of PFSA in PFSA-PVA Coating Solution on PV Performance of PFSA-PVA/PSf Hollow Fiber Composite Membranes by Both Heat Treatment and Chemical Crosslinking Method

Membrane no.	α	J (L m^{-2} h^{-1})	PSI (L m^{-2} h^{-1})	δ (μm)
M14-1	362	128	46,340	8.0
M24-1	340	124	42,160	2.0
M34-1	418	90	37,620	4.0
M44-1	498	75	37,350	9.0
M54-1	125	269	33,630	2.5

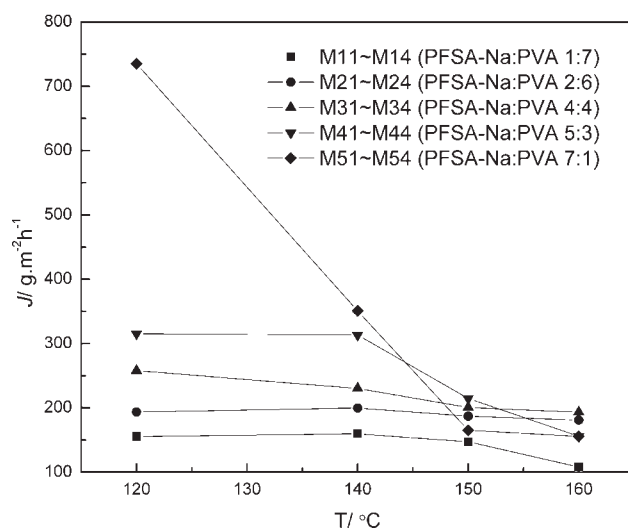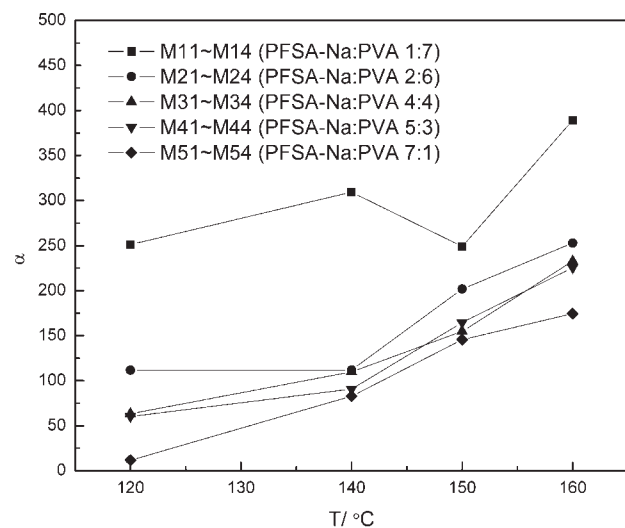PV conditions: 95% IPA; temperature 40°C.

Figure 2 Effects of heat treatment temperatures on PV performance of PFSA-PVA/PSf hollow fiber composite membranes by heat treatment method (PV conditions: 95% IPA; temperature 50°C).

composite membranes strongly depend on heat treatment temperature. With an increase of heat treatment temperature, the separation factors of all composite membranes with different coating layers increase and the total permeation fluxes of the membranes decrease. PFSA membrane obtained from room evaporation in small molecular solvent reveals an amorphous structure. It has poor mechanical strength and is soluble in hot water and many polar solvents. But heat treatment at high temperature in air or under vacuum can make it crystallize and be insoluble.[30,31] With the increment of heat treatment temperature, more energy was provided to produce a higher crystallinity. The cluster network model of PFSA proposed by Gierke[32,33] gave a reasonable account for PV process of PFSA membrane. During

the annealing process (heat treatment), the main chains containing $—CF_2—$ gradually crystallize, the $—SO_3^-$ and counterions form ion-clusters. The ion-cluster structure, which is very hydrophilic, forms a channel preferential for water to alcohol. With the increment of heat treatment temperature, the channel gradually forms and the amorphous structure of main chains which do not act with water crystallize gradually. The crystallization structure hinders the pass of permeates. PVA also crystallizes partially during the heat treatment process. The crystallization morphology of polymer causes a decrease of the free volume and restricts the swelling in solution. It results in a lower permeation flux.

Effect of mass fraction of PFSA on PV performance

The PV performances of fibers M14–M54 with different ratios of PFSA to PVA under 160°C were shown in Table III. The top layer thickness of the composite membranes was also listed in Table III. The membrane thickness was estimated on the basis of the SEM pictures in Figure 3. As shown in Table III, the mass fraction of PFSA in the PFSA-PVA coating solution greatly affects the PV performance of hollow fiber composite membrane. The composite membrane (M14) containing 1 : 7 ratio of PFSA to PVA has the highest separation factor of 389. With the increment of PFSA mass fraction, the separation factor decreases. At the ratio of 7 : 1 for M54, the separation factor is 175. The fibers with the highest mass fraction of PFSA have the lowest separation factor. The experimental results reveal that the addition of PVA in the PFSA-PVA coating solution improves the separation factor of composite membranes. Based on the ion-cluster network model proposed by Gierke and Munn,[32] heterogeneous phase structure containing the hydrophilic areas of ion-clusters and the hydrophobic areas of main chains exist in PFSA polymer. The hydrophobic areas of PFSA do not absorb water. Compared to PFSA material, PVA is more hydrophilic and beneficial to preferential absorption and passage of water. Thus, a higher PVA content in dense layer leads to an increase of the separation factor. The flexible PVA may pack the rigid structure of PFSA and lead to a relative low flux.

The dense layer thickness and skin layer composition are two important impacting factors for PV membrane. Ordinarily, a higher membrane thickness causes a lower permeate flux and a higher separation factor. As seen in Table III, M14 and M44 had a smaller permeation flux and a higher separation factor. On the contrary, membranes M24 and M54 had a higher permeation flux. However, the PSI data of five kinds of PFSA-PVA/PSf hollow fiber composite
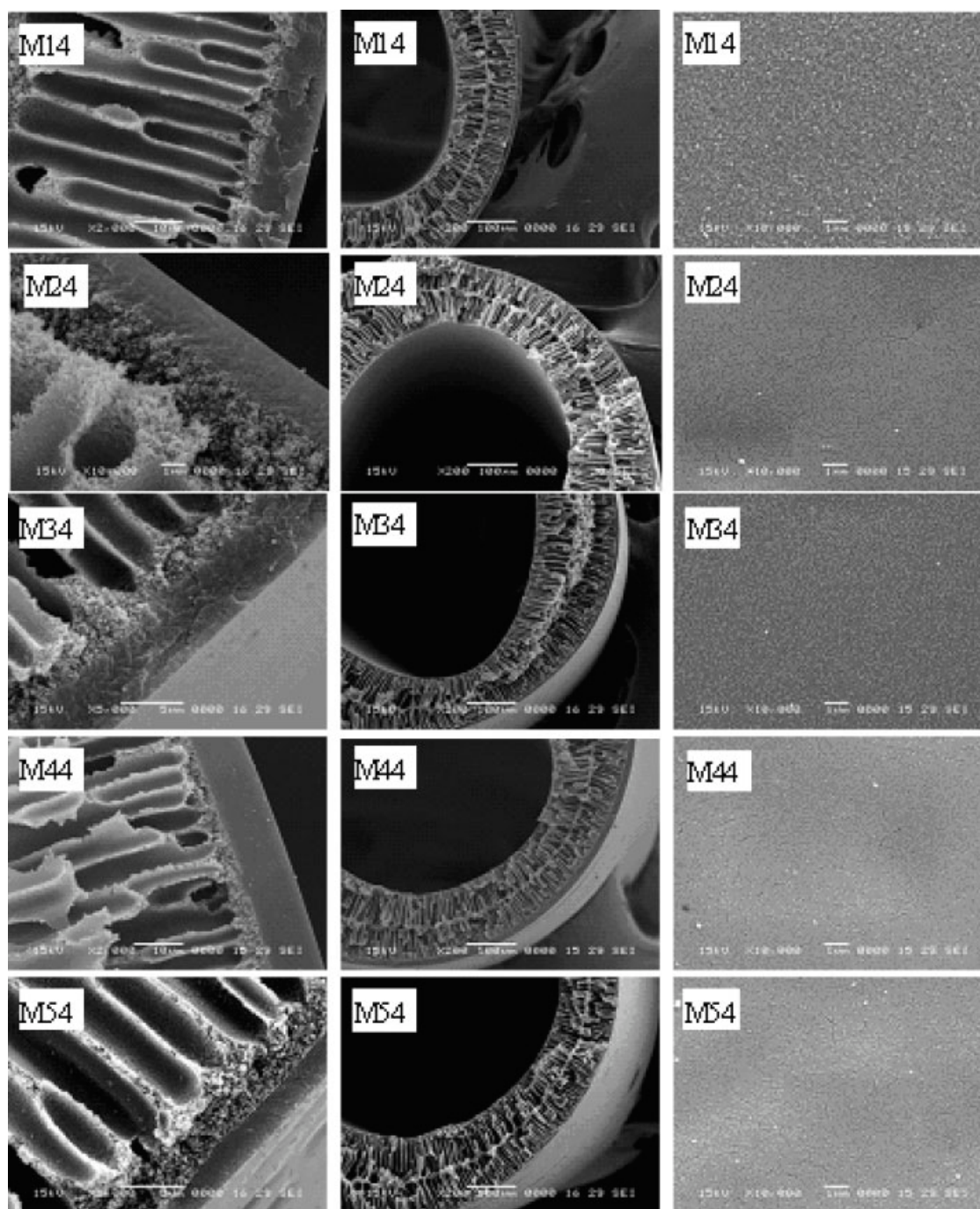
Figure 3 Membrane structures of PFSA-PVA/PSf hollow fiber composite membranes by heat treatment method using different ratios of PFSA to PVA in PFSA-PVA coating solution.

membranes (M14, M24, M34, M44, and M54) only had a little variation in Table III.

The membrane morphology of cross sections and external surfaces of composite membranes with different ratio of PFSA to PVA was shown in Figure 3. As seen in Figure 3(B), the substrate membranes have a bilayer finger-like structure from the fiber pictures for the cross sections. The coating layers with the thickness of about 2–10 μm were clearly found on the pictures for near outer surfaces. The

SEM pictures also reveal that the outer surfaces of all membranes are very dense, but the mass fraction of PFSA in PFSA-PVA coating solution has some slight effect on the membrane surfaces. As the PFSA concentration was low, the membrane surface was rough. With the increment of PFSA concentration, the membrane surface changes to be smooth gradually, but some cracks appear on the membrane surface. PFSA film cast from low boiling point solvent is brittle,[34] while PVA is generally regarded as a

flexible polymer. Therefore, an increase of the mass fraction of PFSA in PFSA-PVA coating solution weakens elastic property of membrane and results in the emergence of some cracks. These cracks also may be the reason for the decline of the separation factor.

Effect of feed temperature on PV performance

Feed temperature is an important operating parameter for PV process. The effect of feed temperature on the separation factor and total permeation flux for the composite membranes M14–M54 are shown in Figure 4. As shown in Figure 4, it has some differences among the composite membranes with different ratios of PFSA to PVA. An interesting phenomenon was found that the effect of feed temperature on total permeation flux of the fibers with a higher mass fraction of PFSA (the ratios of 7 : 1, 5 : 3, and 4 : 4) in the PFSA-PVA coating solution was not more evident than the fibers with a lower mass fraction of PFSA (the ratios of 1 : 7 and 2 : 6). Also, the separation factors of the fibers with the higher mass fraction of PVA were more sensitive than those of the fibers with lower mass fraction of PVA. The addition of PVA would increase the sensitivity of both separation factor and flux to feed temperature. Usually, the separation factor decreases and total permeation flux increases with an increase of feed temperature for PVA PV membrane. However, the separation factor of PFSA PV membrane remains unchanged with the variations of feed temperature.[13]

PFSA-PVA/PSf hollow fiber composite membranes post-treated by both heat treatment and chemical crosslinking

Although the composite membranes post-treated by heat treatment had a favorable separation factor and flux, the coating layer swelled in some content during PV process and some cracks on their membrane surfaces also lead to a decline of separation factor. Chemical crosslinking is a better method to solve the problems, especially for PVA materials. Besides, chemical crosslinking would lead to a denser surface and a better separation performance of the membranes. The following discussions were aimed at the composite membranes, which were post-treated by first heat treatment at 160°C and then chemical crosslinking under different conditions.

Effects of mass fractions of PFSA on PV performance of the composite membranes

The composite membranes (M14-1 to M54-1) with different compositions of PFSA-PVA coating solutions were chemically crosslinked in 4% crosslinking
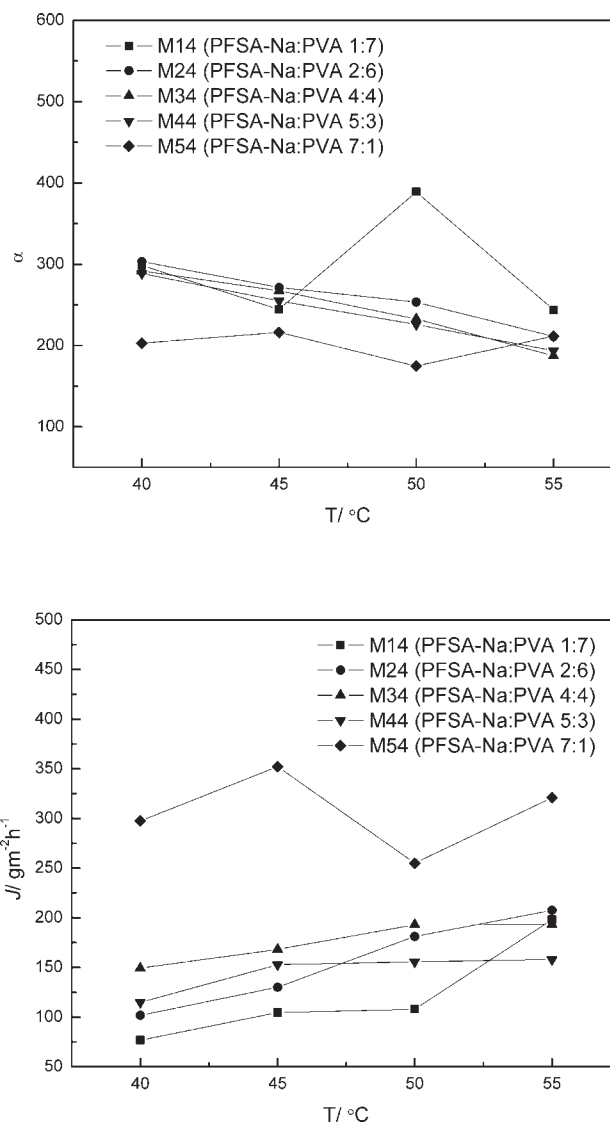
Figure 4 Effects of feed temperatures on PV performance of PFSA-PVA/PSf hollow fiber composite membranes by heat treatment method (PV conditions: 95% IPA).

agent solution for 2 h at 40°C (Table IV). As shown in Table IV, the membrane thickness was as same as that of Table III because it neglected the influence of chemical crosslinking on the thickness of dense layer. In Table IV, the separation factor increases with the increment of PFSA mass fraction in PFSA-PVA coating solution and the highest value is 498 for M44-1. Chemical crosslinking could also improve the separation factors of the composite membranes compared with those of the membranes by heat treatment. The separation factors of the composite membranes by both heat treatment and chemical crosslinking method were more than 340 except M54-1 (Table IV), whereas the separation factors of the membranes by heat treatment method were less than 340 except M14 (Table III). The chemical reaction between PVA and MAC is shown in Figure 5.

Figure 5 The chemical crosslinking reaction between PVA and MAC.

A crosslinking network structure could be formed by the first kind of reaction products. Although the other reactions produce two products, they did not prevent the formation of the crosslinking structure. The crosslinked PVA could bind the PFSA chains and make the top layer denser. It could result in an increase of the separation factor. The hydrophilic property of PVA may be weakened for the decrease of its hydroxide radical during chemical crosslinking. Therefore, there are two opposite influences on the separation factor. When mass fraction of PVA in the PFSA-PVA coating solution was higher (PFSA : PVA = 1 : 7), the separation factor has a little decrease. When the mass fraction of PVA in the PFSA-PVA coating solution was lower (PFSA : PVA = 7 : 1), the influence of chemical crosslinking were very weak and results in a little variation of separation factor.

As seen in Table IV, the influence of membrane thickness on permeation performances was obvious. M44-1 with the thickest top layer had the lowest total permeation flux and the highest separation factor. PSI values of the composite membranes were also shown in Table IV. The experimental results show that the PSI values decrease with the increment of PFSA in the PFSA-PVA coating solution.

The highest PSI value is more than 46,000 for M14-1, which has a reasonable flux and an acceptable separation factor.

Effect of chemical crosslinking temperature on PV performances of the composite membranes

The composite membranes (M44-1, M44-2, and M44-3) were chemically crosslinked at three different temperatures (30, 40, and 50°C) for 2 h. The experimental results were shown in Table V. The separation factor has a maximum point at 40°C, whereas the maximum flux appeared at 50°C.
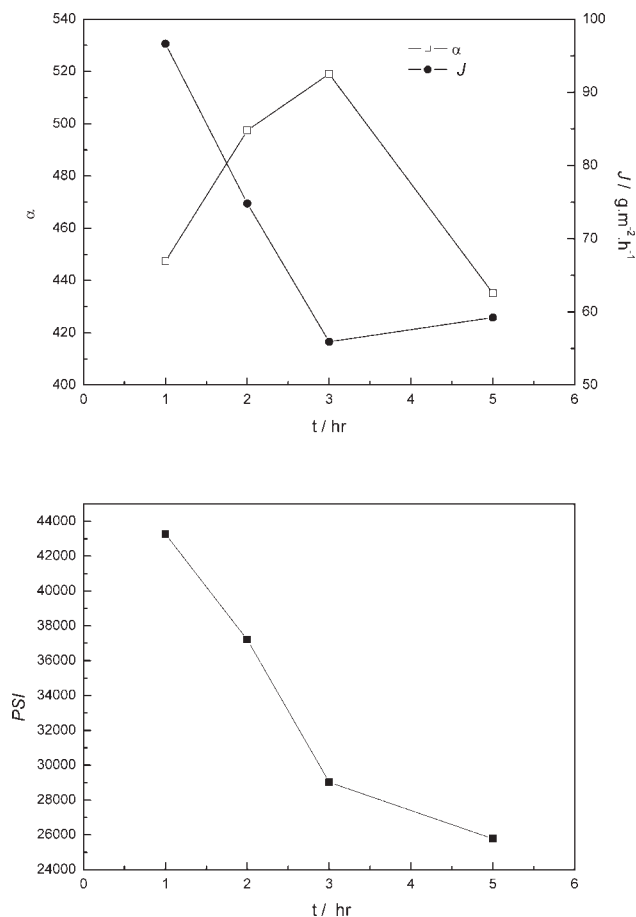
TABLE V
Effect of Chemical Crosslinking Temperature on PV Performance of PFSA-PVA/PSf Hollow Fiber Composite Membranes by Both Heat Treatment and Chemical Crosslinking Method

T (°C)	Membrane no.	α	J (g m^{-2} h^{-1})	PSI (g m^{-2} h^{-1})
30	M44-2	228	97.6	22,170
40	M44-1	435	59.2	25,760
50	M44-3	260	132	34,240

PV conditions: 95% IPA; temperature 40°C.

Figure 6 Effect of chemical crosslinking time on PV performance of PFSA-PVA/PSf hollow fiber composite membranes (M44) by both heat treatment and chemical crosslinking method (PV conditions: 95% IPA; temperature 40°C).

Lower or higher chemical crosslinking temperature could not provide a satisfied separation factor for PFSA-PVA/PSf hollow fiber composite membranes. At a higher temperature, the swelling and dissolution of top blending polymer layer could be aggravated. The swelling would make polymer to be loosened and lead to a decrease of separation factor and an increase of total permeation flux. Another reason may be the dissolution of top layer materials under extra-swelling at higher temperature. A higher temperature could cause the dissolution of the coated layer and a decline of separation factor. But a lower temperature could not provide a desired reaction rate for chemical crosslinking between PVA and MAC. That could be the real reason for the maximum separation factor appearing at 40°C. PSI values presented in Table V has an increase with the increment of chemical crosslinking temperature.

Effect of chemical crosslinking time on PV performance

Figure 6 shows the PV performances of the composite membranes M44-1, M44-4, M44-5, and M44-6, which were chemically crosslinked for different times at 40°C. The maximum separation factor and the minimum total permeation flux appear at 3 h. But the PSI evidently decreases from 43,000 to 20,000, with the increment of chemical crosslinking time from 1 to 5 h. Chemical crosslinking reaction between PVA and MAC causes the skin layer of the composite membranes to be denser. This densification process may lead to an increase of separation factor and a decline of total permeation flux with the increment of chemical crosslinking time before 3 h. However, the separation factor sharply decreases accompanying with a little increase in total permeation flux when chemical crosslinking time exceeded 3 h. It is concluded that as chemical crosslinking time is more than 3 h, chemical crosslinking is unfavorable for the separation performance, especially for the PSI value of the composite membranes.

The SEM pictures of external surfaces of the membranes (M44-1, M44-4, M44-5, and M44-6) by chemical crosslinking for 1, 2, 3, and 5 h were shown in Figure 7. As seen in Figures 3 and 7, the cracks in the external surface were gradually disappeared firstly, but excessive chemical crosslinking time would result in the deterioration of the surface and a decline of separation factor. The external surfaces also reveal that some deposition on the surface results in its roughness, with the increment of PFSA in the PFSA-PVA coating solution (Fig. 8).

CONCLUSIONS

PFSA-PVA/PSf hollow fiber membranes were prepared by dip-coating with PFSA-PVA blend aqueous solution. The membranes were post-treated by heat treatment or by both heat treatment and chemical crosslinking with MAC aqueous solution as crosslinking agent. The composition of PFSA-PVA coating solution, heat treatment temperature, and conditions of chemical crosslinking were investigated. With the increment of heat treatment temperature, the separation factor increased and the total permeation flux decreased. The addition of PVA in PFSA-PVA coating solution was favorable for the improvement of the separation factor of the composite membranes post-treated by heat treatment. Compared with the membranes by heat treatment, the separation factors of the composite membranes post-treated by both heat treatment and chemical crosslinking were evidently improved and reached to be about 520. The membranes post-treated by heat treatment had some cracks and the cracks disappeared after chemical
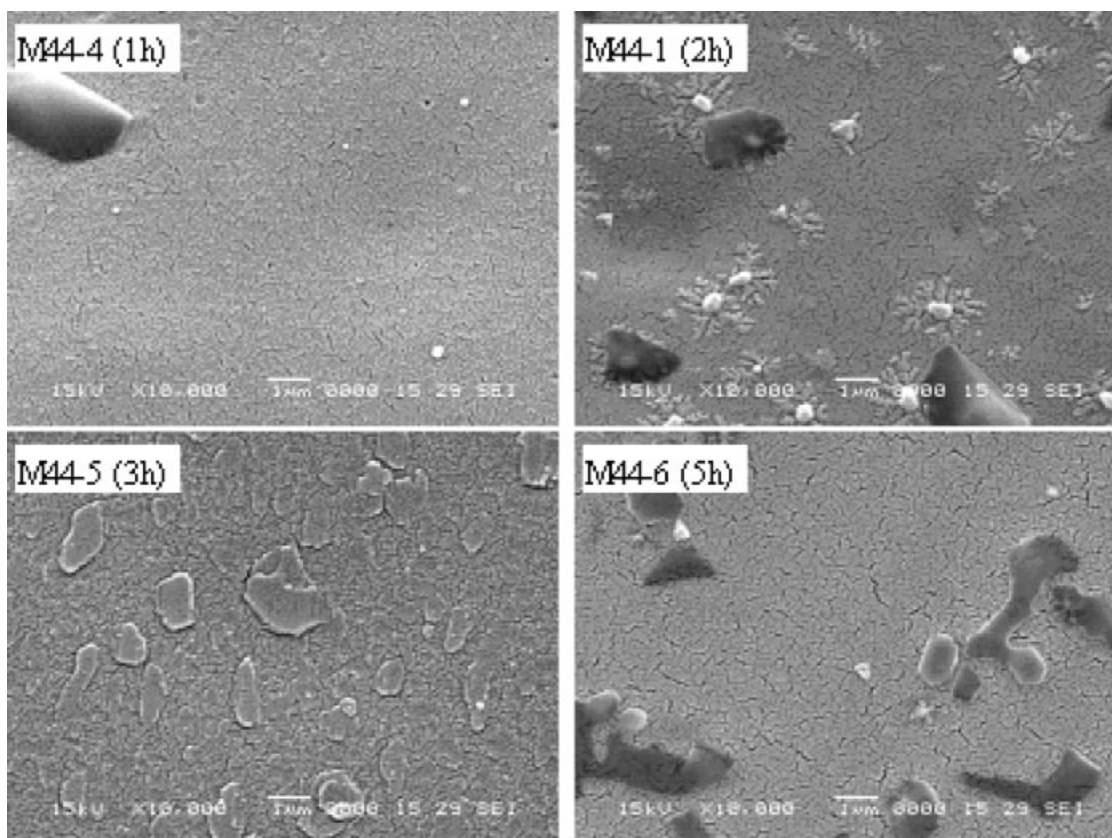
Figure 7 Membrane structures of external surfaces of PFSA-PVA/PSf hollow fiber composite membranes (M44-1, M44-4, M44-5, and M44-6) by both heat treatment and chemical crosslinking method.
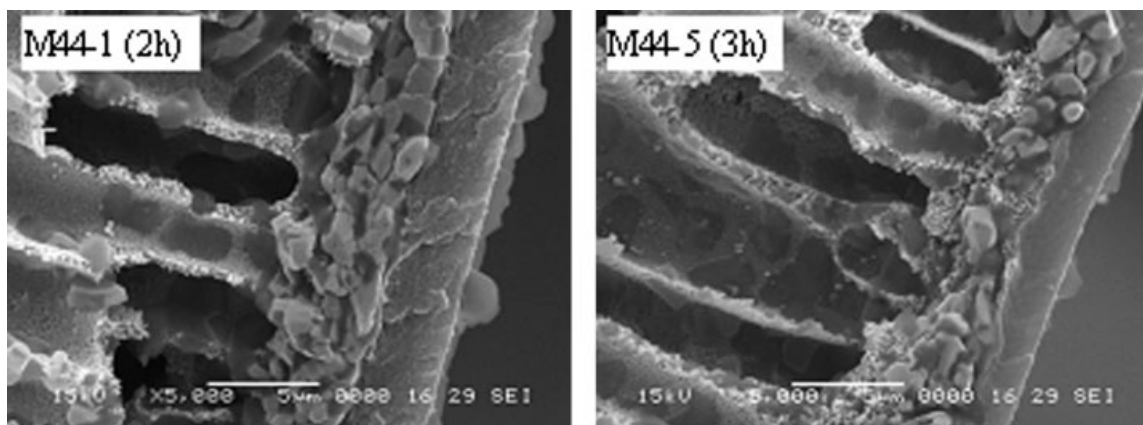

Figure 8 Membrane structures of external surfaces reveal that some deposition on the surface results in its roughness with the increment of PFSA in the PFSA-PVA coating solution.

TABLE VI
The Pervaporation Performances of PFSA Membrane in Ref. 13

Membrane	Nafion 811
a (μm)	90
Counter ion	Na^+
α	25.1
J (g m^{-2} h^{-1})	364

Feed composition IPA/water 88/12%, feed temperature 29°C, Nafion 811 hollow fiber membrane.

crosslinking for a proper time. The experimental results show that the proper preparation conditions for the composite membranes were firstly heated at 160°C for 1 h, followed by chemical crosslinking at 40°C for 3 h. Effect of feed temperature on PV performance had some differences for the membranes with different composition of coating layer. The membranes with the higher mass fraction of PVA in PFSA-PVA coating solution were more sensitive to temperature.

Another point should be emphasized that the separation performances of PFSA membrane were evidently improved by blending with PVA material compared with the homogeneous PFSA PV membrane, as described previously[13] (Table VI).

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