

Effects of Polymerization Conditions on the Properties of Poly(furfuryl alcohol) Composite Membranes

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ABSTRACT: Poly(furfuryl alcohol) (PFA) composite membranes were prepared by polymerization of furfuryl alcohol (FA) using sulfuric acid (H_2SO_4) as the catalyst and polysulfone ultrafiltration membrane as the substrate. The membrane samples were characterized by ATR-IR, TGA, SEM, and gas permeation technique. The effects of synthesis conditions including the FA/ H_2SO_4 molar ratio, polymerization temperature, and the type of solvent on the chemical structure, surface morphology, and gas permeation properties of PFA composite membranes were studied. Our results showed that the suitable synthesis conditions for the preparation of PFA composite membranes with smooth surfaces and uniform structure

include (1) FA/ H_2SO_4 molar ratios: 74–300, (2) polymerization temperatures: 80–100°C, and (3) solvents: ethanol and acetone. The PFA composite membrane prepared with a FA/ H_2SO_4 molar ratio of 250, a polymerization temperature of 80°C and ethanol as the solvent exhibited the highest H_2/N_2 ideal selectivity ($\alpha_{\text{H}_2/\text{N}_2} = 24.9$), and a H_2 permeability of 206 Barrers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3383–3391, 2012

Key words: poly(furfuryl alcohol); polymerization; composite membrane; characterization; gas permeation

INTRODUCTION

Poly(furfuryl alcohol) (PFA) is a common thermally cross-linked polymer that is usually synthesized by the cationic condensation of its monomer furfuryl alcohol (FA).¹ PFA has found a range of applications, such as foundry cores and molds, corrosion-resistant materials, and adhesives.^{2,3} It is also widely used as a precursor to synthesize nanostructured carbons and polymer nanocomposites for adsorbents, separation membranes, catalysts, and electrodes and membranes of fuel cells, lithium batteries, and electric double-layer capacitors, etc.^{1,4–6}

It is well known that the polymerization of FA via acid catalysis is very complex, and the resulting polymer is black in color, amorphous, and cross-linked.^{1,7} The type and initial concentration of the catalyst such as acids and iodine, polymerization temperature and the type of solvent have significant influence on the polymerization process. Therefore, the polymerization kinetics can be varied considerably for specific applications.^{4–6,8–11}

PFA composite membrane was prepared by the polymerization of FA on a porous polymer substrate using sulfuric acid as the catalyst, and it showed good water flux and high salt rejection in the reverse osmosis (RO) desalination process that is one of the most common techniques for producing fresh water from seawater and brackish water for human consumption and industrial uses.¹² Unfortunately, PFA composite membrane was shown to be very sensitive to chlorine and other oxidants involved in the RO process.¹³ Very recently, we modified PFA composite membrane via partial carbonization using the concentrated sulfuric acid treatment, and the resulting carbonaceous PFA composite membranes showed improved chlorine stability in water desalination.¹⁴ However, more research is needed to understand how the structures and morphologies of PFA composite membranes affect the properties of the carbonaceous PFA composite membranes for practical desalination application.

The objective of the present work is to study the effects of polymerization conditions including initial concentration of the acid, polymerization temperature, and the type of solvent on the chemical structure and morphology of PFA composite membranes. To achieve this objective, the chemical structure and morphologies of PFA composite membranes were characterized by ATR-IR, TGA, and SEM. In particular, single gas permeation experiments were carried out to study the permeation property of PFA composite membranes. It is well known that gas

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permeation behavior of polymers is closely related to their chemical structure and microstructure, and their gas permeation properties are vital for many applications such as gas separation membranes and gas-barrier films.^{15,16} It has been shown that the chain-packing density, the degree of crosslinking and the amount of free volume strongly affect diffusivity and solubility of gas molecules in polymers.¹⁵ In addition, it is very difficult to identify the exact chemical structure of PFA produced under different polymerization conditions because of complex reactions.⁴ Therefore, the gas separation technique is used to gain insights into how the PFA structure changes with different polymerization conditions in this work.

EXPERIMENTAL

Preparation of PFA composite membranes

A polysulfone ultrafiltration membrane (GE Osmonics Polysulfone UF ER Membrane, 30,000MWCO, Sterlitech) was used as the support. A piece of dried polysulfone ultrafiltration membrane ($25 \times 70 \text{ mm}^2$) was sealed on the top of a glass slide using a tape to prevent the membrane from rolling up and solution penetration through the edges. Then a FA solution prepared by mixing FA (98%, Sigma-Aldrich), sulfuric acid (98%, Sigma-Aldrich) with solvent (ethanol) was cast on the polysulfone membrane substrate for 5 min at room temperature. After that, the membrane was held in a vertical position for 5 min to drain excessive FA solution. The coated support was then heated at a temperature ranging from room temperature to 100°C overnight for FA polymerization. Six membranes with different FA/ H_2SO_4 molar ratios (i.e., 74, 150, 200, 250, 300, and 400) were prepared by polymerization at 80°C overnight, and denoted PFA-074, PFA-200, PFA-300, and PFA-400. Typically, in the fabrication of PFA-074 membrane, a mixture with a FA/ H_2SO_4 molar ratio of 74 was prepared by dropwise adding 10 g (0.1 mol) of FA into a solution containing 0.135 g (0.0014 mol) of H_2SO_4 and 10 g (0.217 mol) of ethanol. After solution casting, the final membrane was produced by heating at 80°C overnight. Other membranes (PFA-150, PFA-200, PFA-250, PFA-300, and PFA-400) were synthesized using the same procedures except that the FA/ H_2SO_4 ratio was varied.

Four membranes with a FA/ H_2SO_4 molar ratio of 250 were prepared at different polymerization temperatures (20, 45, 80, and 100°C) and denoted as PFA-20C, PFA-45C, PFA-80C, and PFA-100C, respectively). To study the solvent effect, the same amounts of water or acetone were used to replace ethanol, and thus two PFA composite membranes with a FA/ H_2SO_4 molar ratio of 250 were prepared

TABLE I
Summary of PFA Composite Membranes Prepared under Different Conditions

Sample	FA (mol)	FA : H_2SO_4 (mol)	Temperature ($^\circ\text{C}$)	Solvent
PFA-074	0.1	74	80	Ethanol
PFA-200	0.1	200	80	Ethanol
PFA-250 (or PFA-80 or PFA-ethanol)	0.1	250	80	Ethanol
PFA-300	0.1	300	80	Ethanol
PFA-400	0.1	400	80	Ethanol
PFA-20C	0.1	250	20	Ethanol
PFA-45C	0.1	250	45	Ethanol
PFA-100C	0.1	250	100	Ethanol
PFA-water	0.1	250	80	Water
PFA-acetone	0.1	250	80	Acetone

at a polymerization temperature of 80°C . According to the type of solvent used, the PFA composite membranes were denoted as PFA-ethanol, PFA-water and PFA-acetone, respectively. All samples are summarized in Table I.

Characterization

ATR-IR

The samples were characterized using attenuated total reflectance infrared (ATR-IR) spectroscopy. The ATR-IR spectra were recorded at 32 scans at 4 cm^{-1} resolution and in the spectral range of 4000 to 650 cm^{-1} using a Perkin Elmer Fourier-Transform infrared spectrometer with a GX Spectrometer using a ZnSe crystal at an incidence angle of 45° . The active layer of dry PFA composite membrane specimens was mounted on ZnSe crystal facing the crystal surface.

TGA

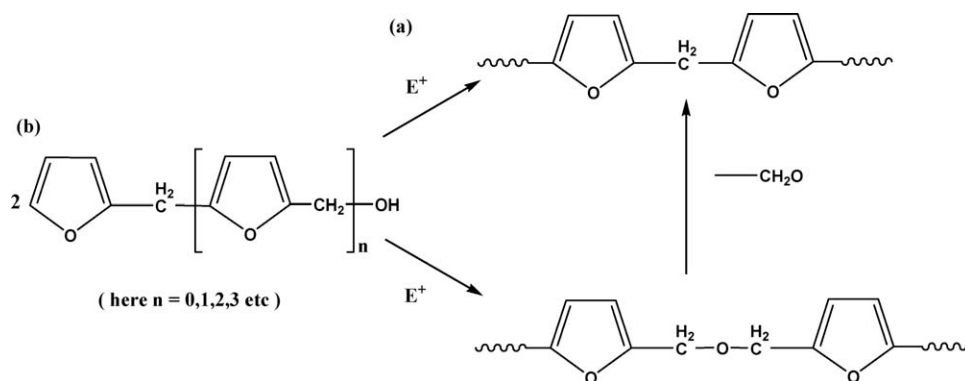
To evaluate the thermal stability of the PFA, thermogravimetric analysis (TGA) was conducted using a thermogravimetric analyzer (TGA, Perkin Elmer) operated in the temperature range of $20\text{--}700^\circ\text{C}$ under nitrogen gas and a heating rate of $5^\circ\text{C}/\text{min}$.

SEM

All scanning electron microscopy (SEM) images were taken with a FEG-7001F microscope (JEOL) operated at an accelerating voltage of 15 kV.

Gas separation

The single gas permeation of membranes was measured using the pressure rise method, and the experimental procedures were detailed in Ref. 17. Briefly, to measure the gas permeation rate, a piece of flat



Scheme 1 Formation of poly(furfuryl alcohol) by acid-catalyzed polymerization of furfuryl alcohol.

membrane was fixed on a stainless steel sample holder using a Varian Torr Seal[®] vacuum sealant. Then it was placed inside a larger Pyrex tube with a feed gas flowing through, and connected to a MKS 628B Baratron pressure transducer and a vacuum pump. For each single gas measurement, the permeate side was vacuumed for around half an hour, allowing enough time to reach steady-state permeation condition; the permeate pressure was maintained at around 2 torr. The permeate stream was then shut off from vacuum and the pressure build-up of the permeating gas was recorded by the pressure transducer.

The molar flow rate (N_i) of the permeating gas was calculated from the linear pressure rise, and its coefficient was calibrated using a digital flowmeter (ADM2000, Agilent, California, USA).

The PFA composite membrane samples were dried at 80°C overnight before the gas permeation test. The feed gas is supplied at room temperature and atmospheric pressure. The effective membrane area was 0.95 cm². Membrane permeance, P_i (10⁻¹⁰ mol/m² s pa), was defined as¹⁷⁻¹⁹

$$P_i = \frac{N_i}{\Delta P_i A}$$

where N_i (mol s⁻¹) is the permeate flow rate of component gas i , ΔP_i (Pa) is the transmembrane pressure difference of i , and A (m²) is the membrane area.

The ideal selectivity α_{ij} were calculated from the relation between the permeance of pure i and j gases^{17,18}

$$\alpha_{ij} = \frac{P_i}{P_j}$$

RESULTS AND DISCUSSION

Chemical structure

Many studies have shown that the polymerization reaction of FA is very complex, and it is difficult to

identify the exact chemical structure of PFA. Scheme 1 shows an example that two parallel reactions occur in the formation of PFA oligomers during the polymerization of FA via acid catalysis.⁴

The ATR-IR spectra of PFA composite membranes prepared at different FA/H₂SO₄ ratios are shown in Figure 1. The main characteristic bands for all PFA composite membranes are similar to those reported in the literature.^{4,8,9,11,20,21} The band at 3500 cm⁻¹ arises from OH group of FA. The band at 1714 cm⁻¹ is ascribed to the carbonylic structure that was formed due to the opening of some furan rings. The band at 1420 cm⁻¹ is attributed to aliphatic segments. The presence of -CH₃ terminal groups at 1386 cm⁻¹ signals the formation of conjugated sequences on the polymer backbone. The band at 1320 cm⁻¹ arises from the ring stretching modes of the 2-substituted and 2,3-bisubstituted furan rings. The band at 1100 cm⁻¹ is attributed to C—O stretching. The band at 1038 cm⁻¹ is attributed to aliphatic segments. The band at 884 cm⁻¹ is attributed to out-of-plane deformation of the CH bonds. The band at 793 cm⁻¹ is attributed to 2,5-disubstituted furan rings. The band at 767 cm⁻¹ is attributed to 2,5-disubstituted rings. The bands at 735, 1016, 1071, 1150, and 1510 cm⁻¹ are ascribed to furan rings. When the molar ratio of FA/H₂SO₄ decreases from 400 to 300, the band at 3500 cm⁻¹ disappears, and the band at 1714 cm⁻¹ is substantially weakened; whereas the intensities for the bands at 1038 and 767 cm⁻¹ decrease. This indicates that PFA-300 has significantly higher degree of polymerization and cross-linking density than PFA-400. However, there is no noticeable difference among PFA-300, PFA-200, and PFA-074, suggesting that the polymerization of FA is probably complete at a FA/H₂SO₄ ratio of 300, and a further increase in the amount of H₂SO₄ does not change PFA structure.

Figure 2 shows the ATR-IR spectra of PFA composite membranes prepared at different polymerization temperatures. The band at 3500 cm⁻¹ becomes weakened as the temperature increases from 20 to 45°C, and it disappears when the temperature

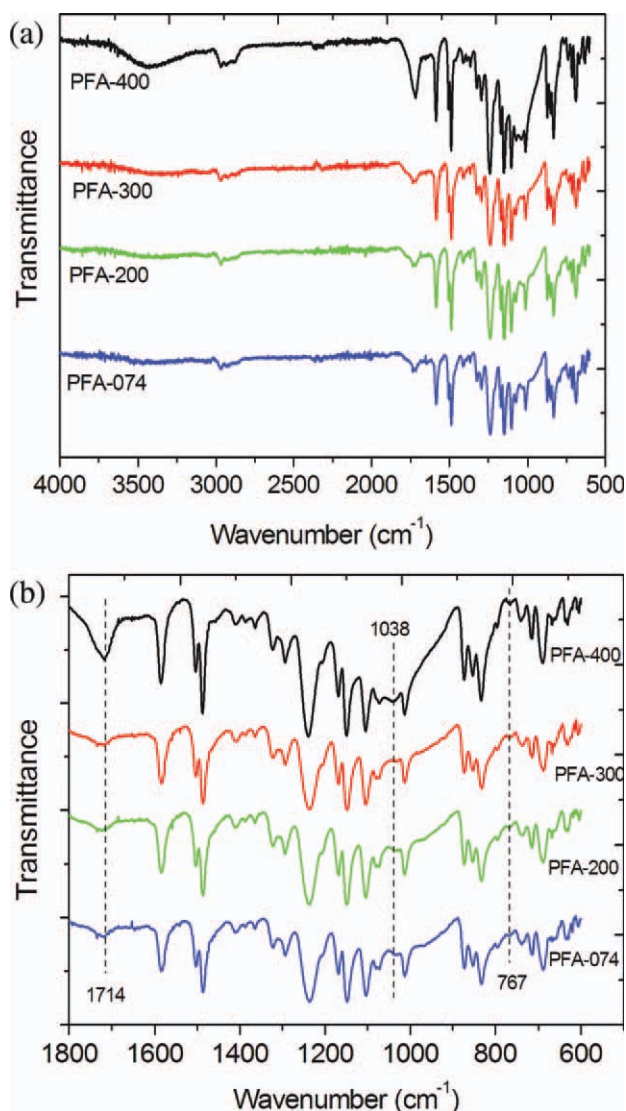


Figure 1 ATR-IR spectra of PFA composite membranes prepared with different FA/H₂SO₄ molar ratios: (a) in the range of 4000–600 cm⁻¹, and (b) in the range of 1800–600 cm⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaches 80°C; meanwhile, the bands at 1038 cm⁻¹ (aliphatic segments), 1714 cm⁻¹ (carbonylic structure), and 921 cm⁻¹ (2-substituted furans²²) are weakened, or even disappear. This indicates that the degree of polymerization of FA increases with increasing the polymerization temperature. In addition, there are no noticeable differences between the ATR-IR spectra of PFA composite membranes prepared with different solvents (i.e., PFA-water, PFA-ethanol, and PFA-acetone).

Membrane morphology

The cross-sectional SEM images of a typical PFA composite membrane (PFA-250) are shown in Figure 3. There are three layers in the PFA composite mem-

brane, which are the top PFA layer, the polysulfone layer, and porous support [Fig. 3(a)]. The thickness of the active PFA layer is estimated to be around 2 μm [Fig. 3(b)]. Figure 4 displays the SEM images of surfaces of PFA composite membranes prepared with different FA/H₂SO₄ ratios. The surface of the PFA-074 membrane looks fairly smooth [Fig. 4(a)]. As the FA/H₂SO₄ ratio increases from 200 to 400, the roughness of the membrane surface increases. This implies that FA polymerization becomes less uniform when the amount of the acid in FA solution decreases.

Figure 5 shows the SEM images of the top surfaces of PFA composite membranes prepared with different solvents. PFA-acetone membrane appears smooth whereas PFA-ethanol membrane slightly rough on top surface. In contrast, the surface of

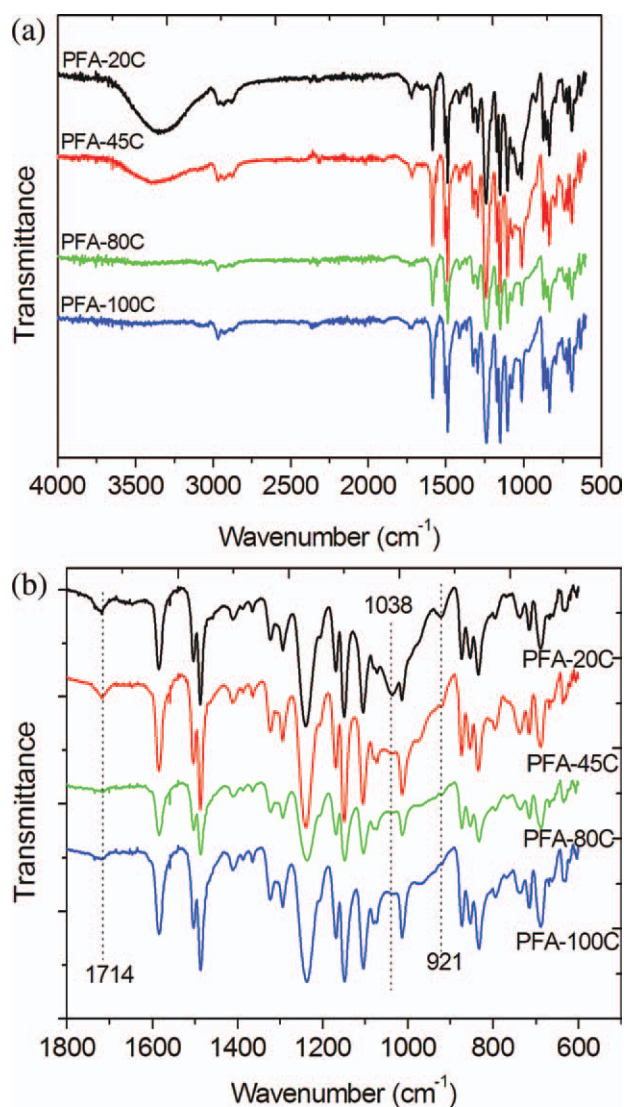


Figure 2 ATR-IR spectra of PFA composite membranes prepared at different polymerization temperatures: (a) in the range of 4000–600 cm⁻¹, and (b) in the range of 1800–600 cm⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

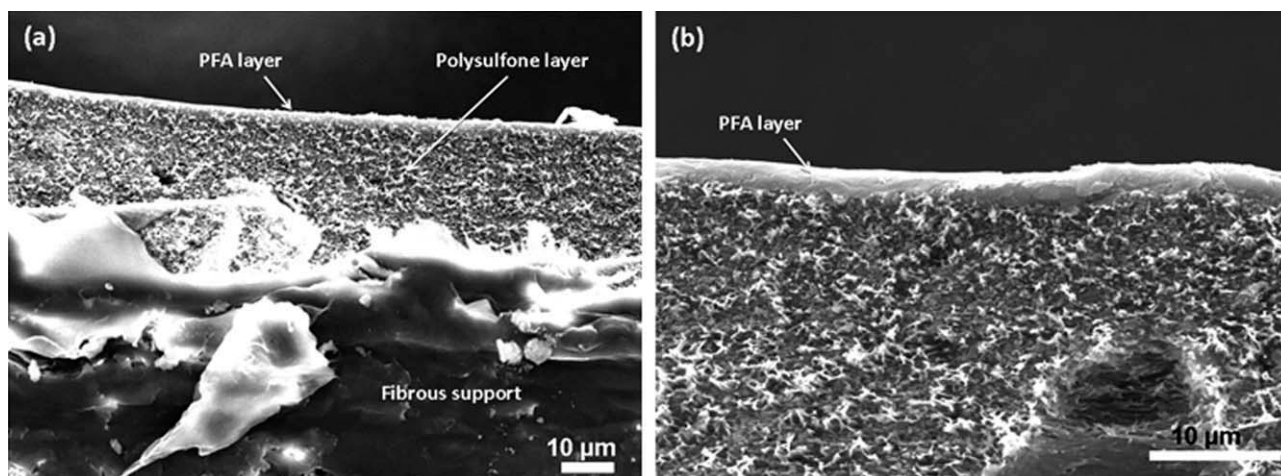


Figure 3 SEM images of the cross section of typical PFA composite membrane: (a) at low magnification and (b) at high magnification.

PFA-water membrane is much rougher than those of PFA-acetone and PFA-ethanol membranes. Such rough surface appearance suggests that PFA phase separation may occur during the polymerization process and solvent evaporation. This is because the vapor pressure (volatility) of water is much smaller than that of ethanol and acetone, and water evaporates much more slowly than the other two solvents. Moreover, PFA is more hydrophobic than FA, and the hydrophobicity of PFA drives its phase separation from water, resulting in a rough surface. The

surface roughness of membranes is closely related to the solvent evaporation rate, and this also explains that PFA-ethanol membrane has slightly rougher surface than PFA-acetone membrane.

Figure 6 shows the SEM images of top surfaces of PFA composite membranes prepared at different polymerization temperatures. As the polymerization temperature increases, the PFA composite membrane surface becomes smoother. This is related to significantly increased rates of FA polymerization and solvent evaporation at high temperatures. These results

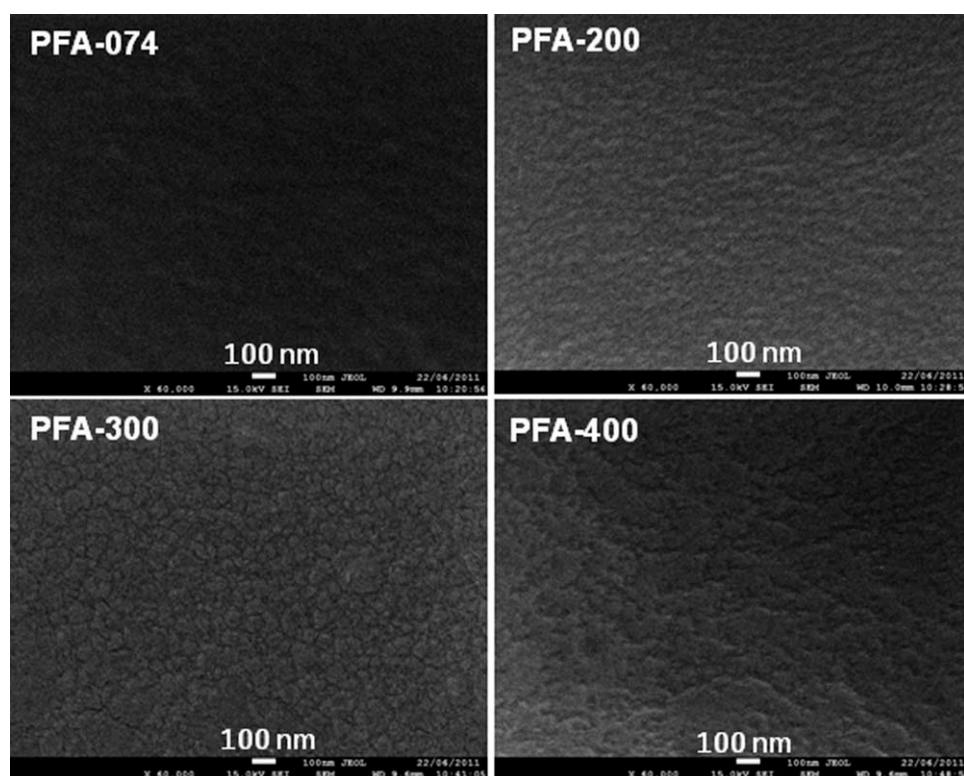


Figure 4 SEM images of top surfaces of PFA composite membranes with different FA : H₂SO₄ ratios.

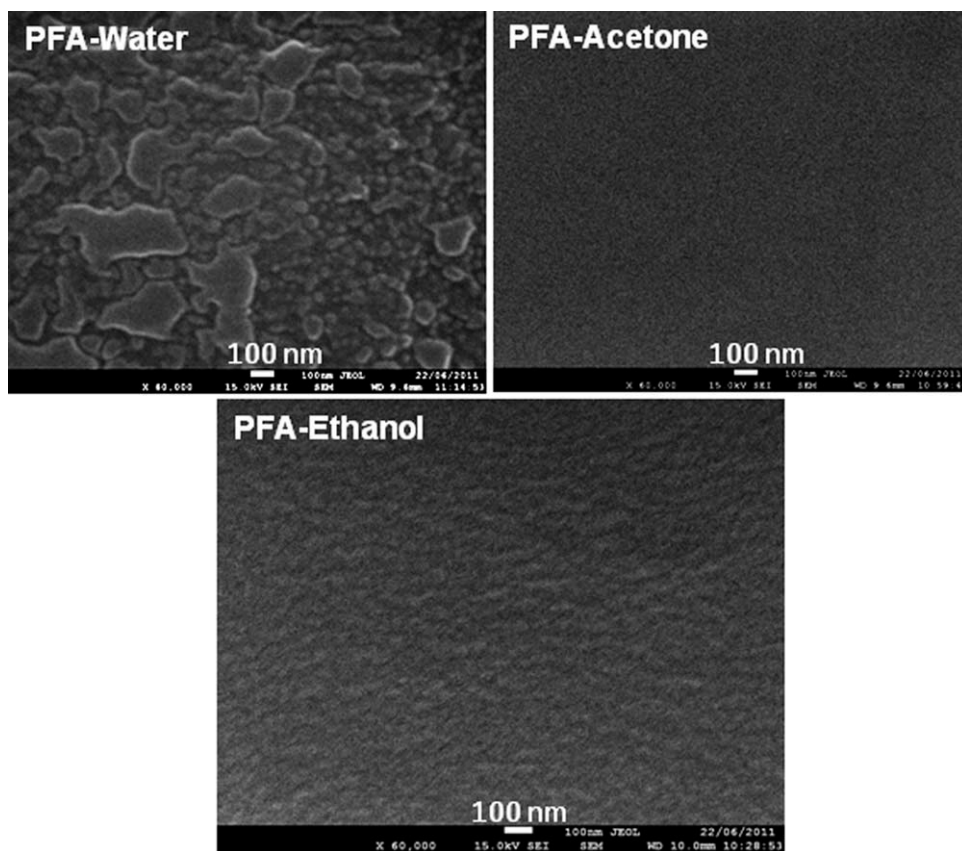


Figure 5 SEM images of top surfaces of PFA composite membranes with different solvents.

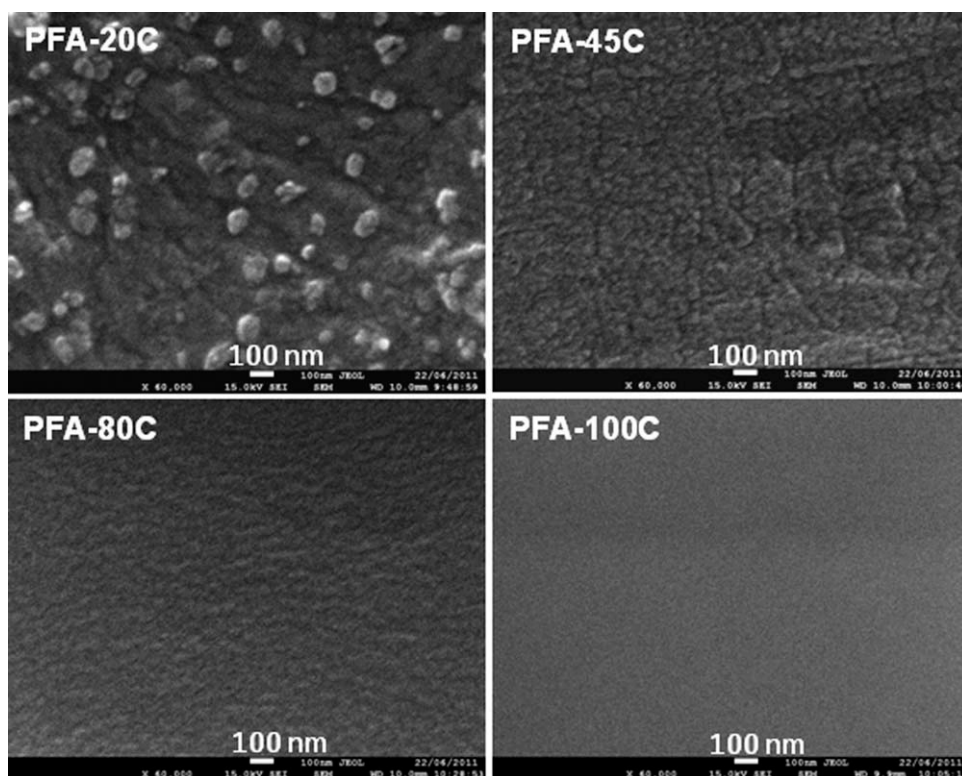


Figure 6 SEM images of top surfaces of PFA composite membranes prepared at different polymerization temperatures.

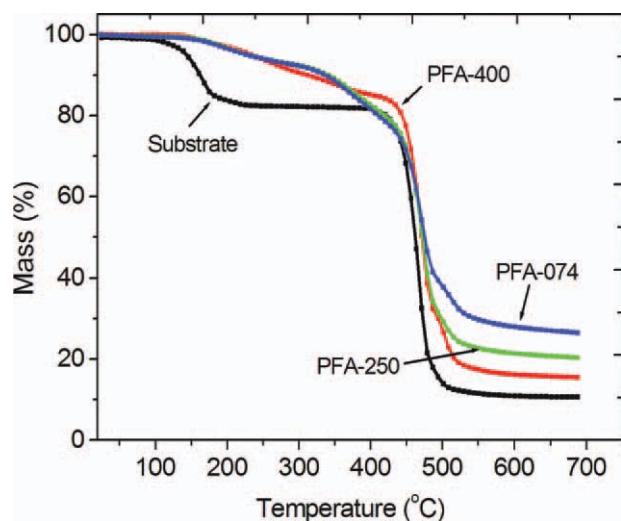


Figure 7 TGA curves of PFA composite membranes with different FA/H₂SO₄ ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicate that the FA to H₂SO₄ ratio, the polymerization temperature and the solvent have significant influence on the morphologies of PFA composite membrane. In our experiments, the suitable preparation conditions for the synthesis of a PFA composite membrane with a smooth surface are identified as follows: PA/H₂SO₄ molar ratios: 74–300, polymerization temperatures: 80–100°C, and solvents: ethanol or acetone.

TGA

The TGA curves of polysulfone membrane substrate and PFA composite membranes prepared with different FA/H₂SO₄ ratios are shown in Figure 7. Under flowing nitrogen, the polysulfone substrate loses 16.1% of its mass in the temperature range from 20 to 200°C. This major mass loss starts from 100°C, corresponding to the evaporation of adsorbed water. In the temperature range of 200–400°C, there is an only 2.3% mass loss, indicating that the substrate has good thermal stability. From 400 to 700°C, a further 70.9% mass loss is observed because of the decomposition of the membrane substrate. The mass losses of PFA composite membranes are much slower than the membrane substrate from room temperature up to around 400°C; their overall mass losses in this temperature range are similar to that of the membrane substrate. This is because the presence of the PFA top layer on PFA composite membranes slows down the evaporation of adsorbed water. All membranes experience a major mass loss from 400°C to 500–550°C, arising from the decomposition of polymers via generation of CO, CH₄, and CO₂²¹; the total mass losses are 89.3, 84.3, 79.0, and

73.3% for the polysulfone membrane substrate, PFA-400, PFA-250, and PFA-074, respectively. This result indicates that the PFA composite membranes prepared with high FA/H₂SO₄ ratios exhibit lower thermal stability. This is consistent with the ATR-IR result that the degree of polymerization and the crosslinking density of PFA decrease as the FA/H₂SO₄ ratio increases.

Figure 8 shows the TGA curves of PFA composite membranes prepared at different polymerization temperatures. The mass losses for both PFA-20C and PFA-45C begin at 100°C; but in the range of temperature of 100–400°C, the mass loss of PFA-20C is more rapid than that of PFA-45C. PFA-80C and PFA-100C appear to be more thermally stable than PFA-45C and PFA-20C. The total mass losses are 90.6, 83.1, 79.6, and 78.9% for PFA-20C, PFA-45C, PFA-80C, and PFA-100C, respectively. This is because higher polymerization temperatures would lead to more crosslinked polymer structures, which exhibit higher thermal stability.

Gas permeation

Single H₂ and N₂ gas permeation experiments were carried out to study gas separation properties of PFA composite membranes prepared under different polymerization conditions. The gas permeation results of PFA composite membrane prepared with different FA/H₂SO₄ ratios are summarized in Table II.

Neither H₂ nor N₂ gas permeation through PFA-074 membrane was detected, suggesting that PFA-074 membrane has extremely low permeance, which is beyond the detection limit (around 1.3×10^{-12} mol/m² s pa). This may be because PFA membrane

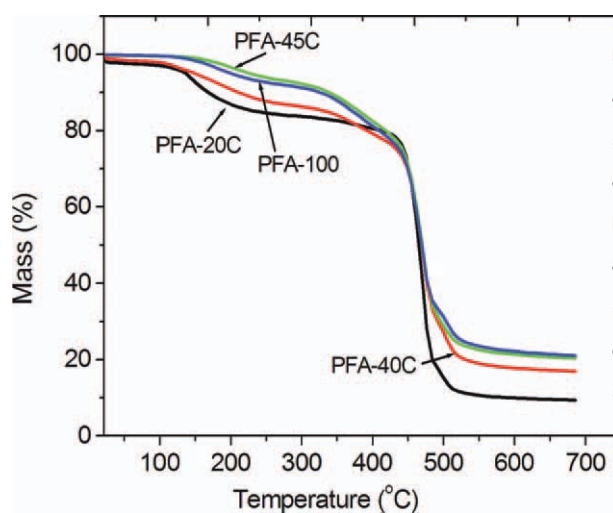


Figure 8 TGA curves of PFA composite membranes with different polymerization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Gas Permeation Results for PFA Composite Membranes Prepared with Different FA/H₂SO₄ Ratios

Sample	FA/H ₂ SO ₄ molar ratio	Permeance (10 ⁻¹⁰ mol/m ² s pa)		Ideal selectivity
		N ₂	H ₂	H ₂ /N ₂
PFA-074	74	0.00	0.00	–
PFA-150	150	0.00	2.2	–
PFA-200	200	8.2	26.3	3.2
PFA-250	250	14.8	369.0	24.9
PFA-400	400	266.4	300.1	1.1

produced at a FA/H₂SO₄ ratio of 74 is highly cross-linked, and PFA chains are densely packed. This result is in good agreement with those reported in literature.^{23,24} For instance, Shiflett and Foley, reported that a PFA layer supported on a porous stainless steel was not permeable to He, H₂, O₂, and N₂ gases.²³ When FA to H₂SO₄ ratio was increased to 150, only H₂ gas permeated through PFA-150 membrane, and no N₂ gas permeation was observed. Both H₂ and N₂ gas permeances largely increased, as the FA/H₂SO₄ ratio was further increased to 400. This may be explained by the change in chemical structure and microstructure of PFA composite membranes. As evidenced from ATR-IR and TGA results, when the sulfuric acid concentration decreases, the degree of polymerization and the crosslinking density of the PFA drop; therefore, the membrane structure becomes more flexible, leading to an increase in gas permeation rates. Furthermore, the microstructure of PFA composite membrane becomes less uniform at higher FA/H₂SO₄ ratios as seen from the SEM results; it is likely that the membranes are defective, resulting in a decrease in gas selectivity. Note that the H₂/N₂ ideal selectivity of PFA composite membrane reaches a maximum of 24.9 at a FA/H₂SO₄ ratio of 250 (PFA-250). The H₂ permeability of this membrane is calculated to be 206 Barrers given the PFA thickness of 2 μm determined by SEM. Compared to the H₂/N₂ upper bond data in the relationship of permeability and selectivity in the Ref.²⁵ The H₂/N₂ separation characteristics of PFA-250 membrane are close to the prior upper bond, suggesting that PFA-250 membrane has a good H₂/N₂ separation property. The good H₂/N₂ selectivity seen in PFA-250 might be related to high H₂ diffusion coefficient because of more ether-bridge structure formed in this membrane despite the exact PFA structure is still unclear.

Table III lists N₂, H₂ permeances and H₂/N₂ selectivity of the PFA-water, PFA-ethanol, and PFA-acetone membranes. There is little difference in the N₂ permeance between PFA-ethanol and PFA-acetone membranes. PFA-water has much higher N₂ perme-

TABLE III
Gas Permeation Results for PFA Composite Membranes Prepared with Different Solvents

Sample	Solvent	Permeance (10 ⁻¹⁰ mol/m ² s pa)		Ideal selectivity
		N ₂	H ₂	H ₂ /N ₂
PFA-water	Water	82.4	139.3	1.7
PFA-ethanol (PFA-250)	Ethanol	14.8	369.0	24.9
PFA-acetone	Acetone	19.9	111.3	5.6

ance than the other two membranes. This can be explained by the fact that PFA-water membrane has nonuniform structure as shown in Figure 5. The boundaries between aggregates are likely more permeable to slightly large molecules (N₂) than aggregates. Once gain, PFA-ethanol (i.e., PFA-250) membrane shows the highest H₂/N₂ selectivity.

The gas permeation results for PFA-100C, PFA-80C, PFA-45C, and PFA-20C membranes are compared in Table IV. It is clear that as the polymerization temperature increases, both H₂ and N₂ permeances rise greatly. As indicated by the ATR-IR, SEM, and TG results, the increasing temperature leads to a more crosslinked PFA structure, which has a decreasing free volume for gas transport.

CONCLUSIONS

The effects of FA/H₂SO₄ molar ratio, polymerization temperature and solvent on the formation of PFA composite membranes were investigated. The results are summarized below.

1. The FA/H₂SO₄ ratio was varied from 74 to 400 while ethanol was used as the solvent, and the polymerization temperature was fixed at 80°C. The PFA composite membranes prepared with FA/H₂SO₄ ratios of 74–300 had smooth surface, and more crosslinked structures. The N₂ gas permeance of PFA

TABLE IV
Gas Permeation Results for PFA Composite Membranes Prepared at Different Polymerization Temperatures

Sample	Polymerization temperature (°C)	Permeance (10 ⁻¹⁰ mol/m ² s pa)		Ideal selectivity
		N ₂	H ₂	H ₂ /N ₂
PFA-100C	100	2.24	2.46	1.1
PFA-80C	80	14.8	369.0	24.9
PFA-45C	45	361.8	823.1	2.3
PFA-20C	20	577.2	1064.9	1.8

composite membranes increases with decreasing the FA/H₂SO₄ ratio.

2. Three solvents including ethanol, acetone, and water were used to prepare PFA composite membranes, while the polymerization temperature was fixed at 80°C and the FA/H₂SO₄ ratio was set at 250. The use of ethanol or acetone leads to smooth PFA composite membrane surface while the PFA-water membrane appears phase separated. No noticeable differences among these PFA composite membranes were observed by ATR-IR and TGA. The nitrogen permeance of the PFA-water membrane was more than four times higher than those of the PFA-ethanol and PFA-acetone membranes.
3. The polymerization temperature was varied from 20 to 100°C while ethanol was used as the solvent and the FA/H₂SO₄ ratio was fixed at 250. The PFA composite membranes prepared at 80–100°C possessed smooth surface and more crosslinked structures. Furthermore, the membranes produced at low temperatures (i.e., 20 and 45°C) exhibited much higher gas permeances than those prepared at high temperatures (80 and 100°C).

By comparing all membrane samples, the PFA composite membrane prepared with a FA/H₂SO₄ ratio of 250 at 80°C and with the use of ethanol as the solvent showed the highest H₂/N₂ ideal selectivity and a H₂ permeance of 3.69×10^{-8} mol/m² s pa.

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