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Acrylamide plasma-induced polymerization onto expanded poly(tetrafluoroethylene) membrane for aqueous alcohol mixture vapor permeation separation

Chen-Yuan Tu [a], Chiu-Ping Chen [a], Yi-Chieh Wang [b], Chi-Lan Li [b], Hui-An Tsai [c], Kueir-Rarn Lee [a,b,*], Juin-Yih Lai [a]

[a] *R&D Center for Membr. Technol. and Department of Chemical Engineering, Chung Yuan University, Chung Li 32023, Taiwan*
[b] *Department of Chemical Engineering, Nanya Institute of Technology, Chung Li 32034, Taiwan*
[c] *Department of Textile Engineering, Nanya Institute of Technology, Chung Li 32034, Taiwan*

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Abstract

To improve the vapor permeation performance of aqueous alcohol mixtures, acrylamide (AAm) plasma activation then post-graft polymerization onto an expanded poly(tetrafluoroethylene) (e-PTFE) membrane, e-PTFE-g-AAm, was synthesized in this study. The surface properties of the e-PTFE-g-AAm membrane were characterized using ATR/FTIR, SEM, AFM and the water surface contact angle. The degree of grafting increases with increasing polymerization temperature. A maximum value was obtained at 80 °C. The water contact angle of the pristine e-PTFE membrane and the e-PTFE-g-AAm membrane with a 21% grafting degree was 109.7° and 34.1°, respectively. Optimum vapor permeation performance was obtained using an e-PTFE-g-AAm membrane with a 21% grafting degree for a 90 wt.% aqueous ethanol solution, giving a permeate water concentration of 99.4% and a permeation rate of 648 g/m^2 h.

Keywords: Plasma; Expanded poly(tetrafluoroethylene); Post-graft polymerization; Vapor permeation

1. Introduction

Pervaporation and vapor-permeation is a promising membrane separation process for the separation of azeotropic mixtures, heat-sensitive mixtures, mixtures approaching the boiling point, and for the removal of volatile organic compounds in wastewater because of the potential energy cost savings. Thus, many researchers have investigated the separation and permeation characteristics for the above mixture solution using a variety of membranes [1–4]. For organic liquid mixture dehydration through pervaporation or vapor permeation membranes, most researchers have focused on hydrophilic membrane preparations such as poly(vinyl alcohol), chitosan, and their derivatives [5–7]. Because the liquid mixture selectivity through a polymer membrane is a function of the difference in solubility and diffusivity of the solvents, when organic liquid mixtures containing one component that has high solubility for the polymer membrane, membrane swelling by this component leads to a decrease in perm selectivity. To develop high permselectivity membranes for organic liquid mixtures, membrane swelling prevention is very important. Thus, many researchers have focused on improving the membrane solubility for the separation process using plasma grafting, polymer blends, chemical grafting and preparing new polymers [8–11]. Making a careful appropriate material choice for pervaporation is exceedingly important.

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[*] Corresponding author. Address: Department of Chemical Engineering, Nanya Institute of Technology, Chung Li 32034, Taiwan. Tel.: +886-345-35521; fax: +886-343-61747.
E-mail address: krlee@nanya.edu.tw (K.-R. Lee).

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Poly(tetrafluoroethylene) is a potential film material because of its attractive combination of chemical, physical and thermal resistance properties. Because of its high melting point and poor solubility in organic solvents, sintering is a suitable technique for preparing PTFE films. The material is stretched under high temperatures, then sintered, producing a porous organic membrane. However, only micro-filtration membranes can be prepared via sintering. The membrane's porosity is too high to obtain a high selectivity when prepared using stretching methods. The plasma-graft polymerization technique has been widely used to prepare pervaporation membranes for aqueous alcohol mixture separation. Plasma is a mixture of electrons, ions, excited molecules, radicals and energetic photons (UV light), that are able to initiate chemical reactions against polymer surfaces and induce polymerization reactions. The plasma induced graft-polymerization technique is a well known polymer surface modification technique. The plasma induced graft-polymerization technique involves two steps. The first step involves generating active sites (including carbon radicals or peroxides) on the polymer using plasma. The second step involves monomer grafting and polymerization with the active sites. A plasma-polymerized ultra thin film coating permanently changes the surface energy of a substrate without altering the material's bulk properties [12]. For instance, acrylic acid plasma polymerization or of acrylic acid/carbon dioxide mixtures yield carboxylic acid groups onto the surface [13–15]. Currently, the plasma graft polymerization technique is used to modify the surface of expanded poly(tetrafluoroethene) (e-PTFE) membranes to improve the vapor-permeation performance. Polytetrafluoroethene is a membrane with potential for the pervaporation process because of its attractive combination of physical, chemical and thermal resistance properties. Acrylamide (AAm), which has high hydrophilicity, is the grafting material discussed in this work.

The purpose of this study is to prepare plasma graft polymerized acrylamide onto an expanded poly(tetrafluoroethene) membrane for the vapor-permeation process. The plasma grafting polymerization condition effects and feed compositions on the membrane performance were studied. SEM, AFM, ATR/FTIR and the surface contact angle were used to study the changes in membrane morphology, chemical composition and surface hydrophilicity of pristine e-PTFE and the plasma grafted e-PTFE-g-AAm membranes.

2. Experimental

2.1. Materials

e-PTFE sheets used were commercially procured from YMT Co., Ltd. Taiwan. These membranes had a melting point of approximately 327 °C, a mean pore size of approximately 0.4 μm and were 160 μm thick. The sample sheets were prepared using Soxhlet extraction. Acrylamide (AAm) of 99% purity was purchased form Merck Co. The oxygen used for the plasma polymerization was pure grade (99.5% purity).

2.2. Plasma graft polymerization

A tubular type deposition system, externally equipped with capacity coupling electrodes (RFG-300. Samco Ltd., Japan) was used in this study, as shown in Fig. 1. Prior to igniting the oxygen plasma, the pressure in the reactor was evacuated to 10^{-2} Torr. For the experiments, pure oxygen was introduced into the reactor via a gas mass flow controller (MFC) at a flow rate of 10 sccm. Plasma ignition occurred at approximately 1 Torr. The plasma was ignited at a frequency of 13.56 MHz with a supplied power of 50 W for 60 s. The degassed monomer solution was introduced into the tubular reactor followed by the plasma treatment. The tubular reactor was taken off, then placed into a reciprocating shaker at various temperatures for 5 h. Distilled water was used to remove the homo-polymer at 50 °C for 24 h. After homo-polymer extraction, the degree of grafting and grafting efficiency of AAm onto the e-PTFE membrane was calculated according to the following equations:

$$\begin{aligned}\text{Degree of grafting (\%)} &= [(\text{wt. of grafted e-PTFE}) \\ &\quad - (\text{wt. of non-grafted e-PTFE})] \\ &\quad /(\text{wt. of non-grafted e-PTFE})\end{aligned}$$

$$\begin{aligned}\text{Grafting efficiency (\%)} &= [(\text{wt. of produced AAm polymer}) \\ &\quad - (\text{wt. of AAm homopolymer})] \\ &\quad /(\text{wt. of produced AAm polymer})\end{aligned}$$

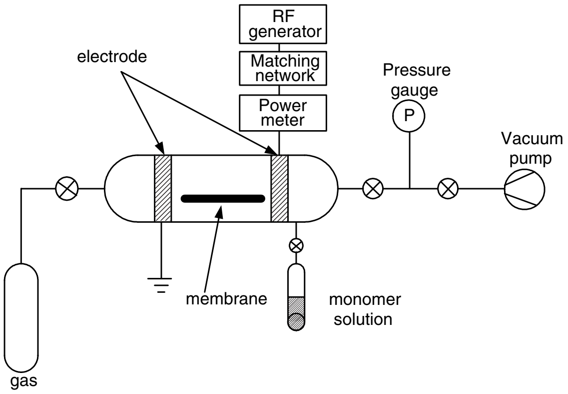

Fig. 1. Plasma deposition apparatus.

2.3. Vapor permeation experiment

A traditional vapor permeation process was used [16]. The feed solution was vaporized first and then permeated through the membrane. The effective area was 2.05 cm^2. In this experiment, the permeation rate was measured using the permeate weight. The feed solution and permeate composition were measured using gas chromatography (GC China chromatography 8700 T). The separation factor was calculated from the following equation:

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

X_A and X_B are the weight fractions of the water and alcohol vapors in the feed (A being the more permeative species). Y_A and Y_B are the weight fractions of the water and alcohol in the permeate.

2.4. Surface and cross-section morphology studies

The surface and cross-section morphology studies were conducted using a scanning electron microscope (Hitachi Model S4700), atomic force microscope (AFM, Digital Instrument, DI 5000), and FTIR–ATR spectrophotometer.

2.5. Surface wettability characterization

The surface wettability of the pristine and plasma grafted e-PTFE-g-AAm membranes were characterized using the surface contact angle of water. The contact angle of water on the modified e-PTFE membranes was measured at room temperature using the sessile drop method using an angle-meter (Automatic Contact Angle Meter, Model CA-VP; Kyowa Interface Science Co., Ltd. Japan). The distilled water was dropped onto at least ten different sites on each sample. The measured values of the contact angles were averaged.

3. Results and discussion

3.1. Plasma treatment condition effect on the surface water contact angle of the e-PTFE membrane

An e-PTFE-g-AAm membrane was prepared using two steps. In the first step the oxygen plasma activated the e-PTFE membrane. The hydrophilic monomer was grafted onto the surface of the e-PTFE membrane in the second step. The influences of the plasma treatment conditions on the membrane surface properties were investigated. The water contact angle experiment was used to estimate the surface hydrophilicity. A lower contact angle value indicates higher hydrophilicity, suggesting that higher peroxide or carbon radicals exist on the membrane surface, thus showing improved grafting polymerization efficiency. The result is shown in Fig. 2. The figure shows that the water contact angles decreased with increasing plasma power up to 50 W. Beyond this power the water contact angle increased. This might be due to peroxide formation, resulting in decreased water contact angles. However, the polymer radicals will react with other polymer radicals, leading to cross-linking at the higher plasma power. This results in increased water contact angles [17]. Moreover, the etching effect on the polymer surface due electron and ion bombardment from the plasma results in increased surface roughness in the e-PTFE membrane. Hence, the water contact angles increased at higher plasma power. The minimum contact angle appeared under 50 W/ 60 s plasma treatment conditions. Consequently, the optimum treatment condition in this experiment was 50 W supply power and 60 s treatment time.

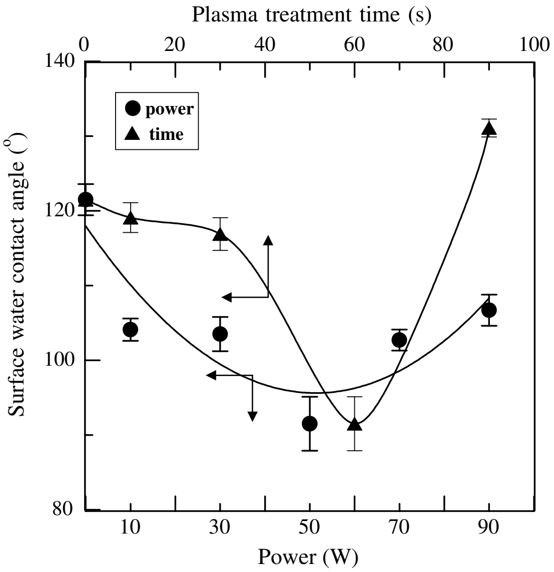

Fig. 2. Effect of plasma treatment conditions on the water contact angle. (●) Plasma treatment time 60 s; plasma power from 10 to 90 W; (▲) plasma treatment time from 10 to 90 s; plasma power 50 W.

3.2. Grafting temperature effect on the degree of e-PTFE-g-AAm membrane grafting

To study the grafting temperature effect on the degree of e-PTFE-g-AAm membrane grafting, the grafting temperature was varied from 50 to 85 °C. Fig. 3 shows the relationship between the grafting temperature and the degree of AAm grafting onto the e-PTFE membrane. The degree of grafting increased with the increase in polymerization temperature up to 80 °C. Beyond 80 °C,

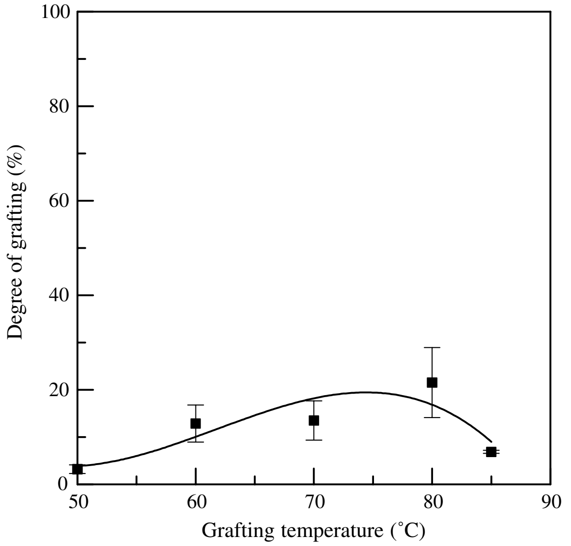

Fig. 3. Effect of grafting temperature on degree of grafting; O_2 plasma 50 W, 1 min, grafting time: 5 h.

the degree of grafting decreased. The grafting efficiency exhibited a similar trend, as indicated in Fig. 4. An increase in polymerization temperature might enhance the rate of polymerization on the substrate membrane surface, resulting in increased probability for creating grafted monomer–polymer chains. In the grafting polymerization system, the monomer is competitive both in grafting and in homopolymerization. A decrease in the grafting degree at 85 °C might be due to homopolymerization playing a more important role than grafting polymerization at higher polymerization temperatures. A maximum value was obtained at 80 °C with 21% grafting degree. Fig. 5 shows the ATR/FTIR spectra for the pristine e-PTFE membrane (a), poly(acrylamide) (b), and e-PTFE-g-AAm membrane (c–g) grafted at various temperatures. On the FTIR spectrum for pristine e-PTFE membranes, strong absorption peaks appeared at 1213 and 1153 cm^{-1} which correspond to the fluorine-containing compound (CF_2, CF_3) of e-PTFE. The e-PTFE-g-AAm membrane spectrum shows a new absorption peak at 1655 cm^{-1}, which is not found in the FTIR spectrum of the pristine e-PTFE membrane. This is due to the carbonyl group of primary aliphatic amides. These results confirm that the AAm monomer is grafting onto the e-PTFE surface through plasma activation, rather than the post-grafting polymerization procedure. In addition, the absorbance (1655 cm^{-1}) increases by increasing the grafting temperature. These results confirm that the AAm monomer is grafting onto the e-PTFE membrane surface, as shown by the results in Fig. 3.

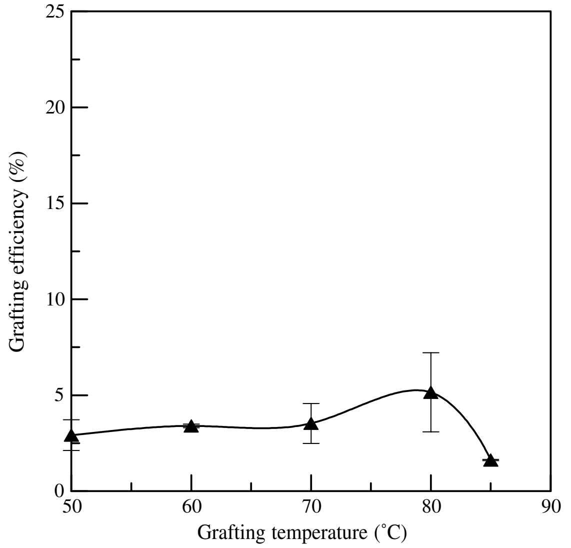

Fig. 4. Effect of grafting temperature on grafting efficiency; O_2 plasma 50 W, 1 min, grafting time: 5 h.

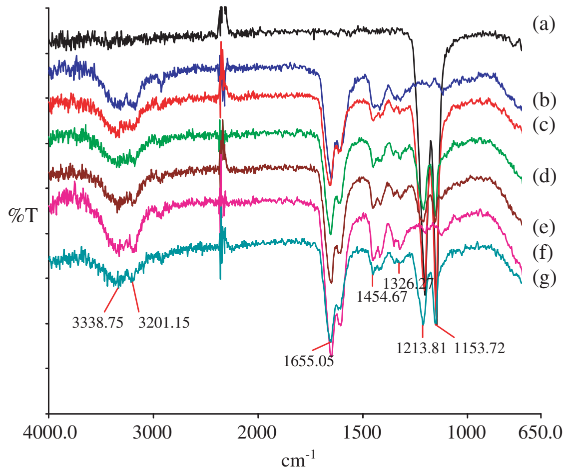

Fig. 5. FTIR ATR spectra of the surface graft of AAm by O_2 plasma onto e-PTFE membrane from various graft temperatures (a) untreated e-PTFE; (b) PAAm; and e-PTFE-grafted-PAAm membranes grafted at (c) 50 °C; (d) 60 °C; (e) 70 °C; (f) 80 °C; (g) 90 °C.

3.3. Degree of grafting effect on the membrane morphology

To evaluate the plasma polymerization effect on the e-PTFE-g-AAm membrane surface structures, the results were further confirmed by AFM analysis and the water contact angle measurement. The water contact angle of a material surface is a function of the surface topography, surface heterogeneity, swelling and superficial reorganization. Wenzel [18,19] developed the first equation relating the surface water contact angle and surface roughness:

$$\cos \theta_{\mathrm{w}} = r \cos \theta$$

where θ_{w} is the contact angle on a rough surface, θ is the contact angle observed on a smooth surface, and r is the surface roughness or the average ratio of the actual to the apparent areas. If θ is less than 90°, then θ_{w} is going to be smaller than θ. Conversely, if θ is greater than 90°, then θ_{w} is going to be greater than θ. The surface roughness can therefore increase or decrease the water contact angle depending on the equilibrium contact angle value on a smooth surface. PTFE surfaces are smooth because of the low polarizability and hydrophobic C–F bond. That is, the water contact angle increases when the surface roughness increases. However, an opposite phenomenon was observed in this investigation. In general, plasma treatment involves two essentially different processes to modify the chemical and physical surface properties [20]. The first process is the functional group reaction, such as carbonyl and carboxyl onto the polymer surface from the radical reactions between radicals in the plasma and polymer surface. The second process is the etching on the polymer surface from electron and ion bombardment from the plasma. The former process increases the hydrophilicity of the e-PTFE membrane. The latter process results in increasing the surface roughness of the e-PTFE membrane. The plasma treatment process impact upon the surface roughness of the e-PTFE membranes was investigated. ESCA was used to analyze the membrane surface composition. The results are shown in Table 1. The plasma modified e-PTFE surface shows a lower F/C atomic ratio and a higher O/C atomic ratio than the original e-PTFE surface. This indicates that the oxygen plasma exposure led to an oxidation reaction on the e-PTFE surface, resulting in increased hydrophilicity. The surface roughness values and AFM photographs are shown in Table 2 and Fig. 6, respectively. It can be seen that the membrane surface structure varies with the different surface treatment techniques. The results also indicate that the surface roughness of the pristine e-PTFE membrane is lower than that of the e-PTFE membrane treated with 50 W/1 min plasma conditions. This may be because an etching effect appears during the O_2 plasma treatment procedure, resulting in increased e-PTFE membrane surface roughness. Furthermore, the surface roughness of the post-grafted AAm monomer onto the e-PTFE membrane treated under 50 W/1 min plasma conditions decreases when compared to the pristine e-PTFE membrane. The AAm layer grafted onto the membrane surface causes the membrane to become denser and smoother. For example, the root mean square surface roughness (R_{ms}) of the pristine e-PTFE surface was about 17 nm. After the O_2 plasma treatment, the surface roughness of e-PTFE film increased to 19.6 nm. For the e-PTFE-g-AAm surface, the surface roughness decreased to about 9.8 nm. This indicates that the surface chemical composition change effect is more important than the increase in surface roughness.Oliver et al. pointed out that the initial surface roughness does not impact the final surface roughness and that the water contact angle depends not only on final surface roughness [21]. To further investigate the grafting effect on the e-PTFE-g-AAm membrane morphology, scanning electron microscopy (SEM) was performed. It is widely accepted that the separation performance of membranes is strongly related to the membrane structure. Therefore, it is reasonable to expect that the membrane structure for the pristine e-PTFE membrane and e-PTFE-g-Aam membrane would be different. SEM micrographs of the surface and cross-section of the pristine e-PTFE membrane and e-PTFE-g-AAm membrane were taken as shown in Figs. 7 and 8, respectively. In Fig. 7, the membrane density increases with increasing grafting degree. Fig. 8 (cross-section views) shows that the AAm graft occur on the surface and sublayer of the e-PTFE membrane. This result indicates that active sites are generated by the O_2 plasma treatment on the surface and the inside pore surface of the e-PTFE membrane. Thus, plasma graft polymerization is an excellent technique for modifying e-PTFE membranes to improve vapor-permeation performance. Moreover, compared with the e-PTFE-g-Aam membrane grafted at 80 °C, the surface of the e-PTFE-g-Aam membrane grafted at 85 °C shows the presence of small pores. These phenomena might be because the rate of homopolymerization is faster than the rate of graft polymerization at higher grafting temperatures, resulting in a decreased grafting layer.

Table 1
Chemical composition of e-PTFE films by oxygen plasma treatment

Sample	Atomic ratio	
	F/C	O/C
Pristine e-PTFE	2.00	0
50 W–60 s O_2 plasma treated e-PTFE	1.96	0.003

Table 2
Surface roughness value of the pristine, O_2 plasma treated e-PTFE, and e-PTFE-g-AAm membrane

Membrane	Ra^{a} (nm)	$R_{\mathrm{ms}}{}^{b}$ (nm)	$R_{\mathrm{MAX}}{}^{c}$ (nm)
Pristine e-PTFE	14.179	16.977	94.236
O_2 plasma treated e-PTFE	15.713	19.628	139.60
e-PTFE-g-AAm-80 °C	7.634	9.796	52.904

[a] Root mean square (RMS) of z values.

[b] Mean roughness.

[c] Mean difference between the five highest peaks and the five lowest values.

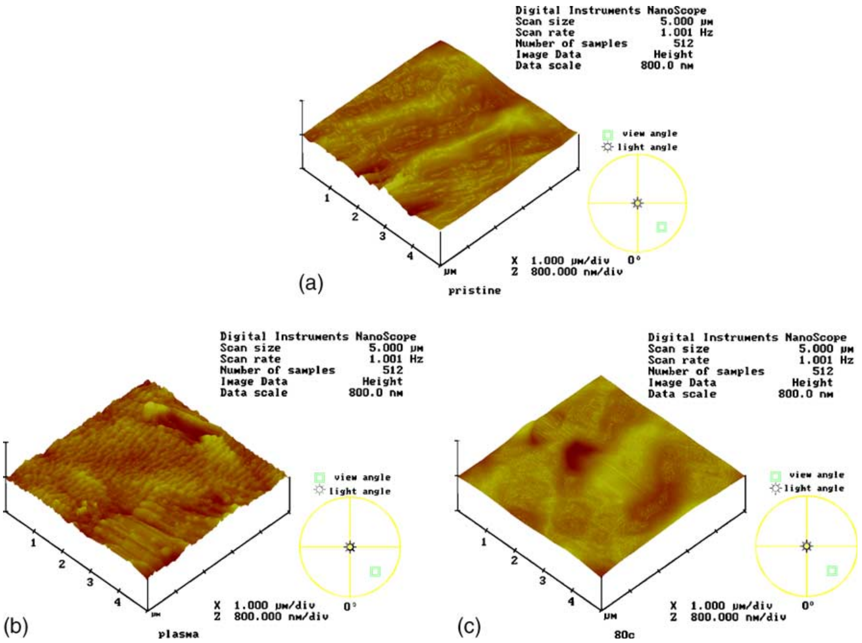

Fig. 6. The AFM image of e-PTFE membrane surface after plasma treatment and post-grafting acrylamide (a) pristine e-PTFE; (b) plasma treatment for 1 min; (c) e-PTFE 80 °C grafted PAAm.

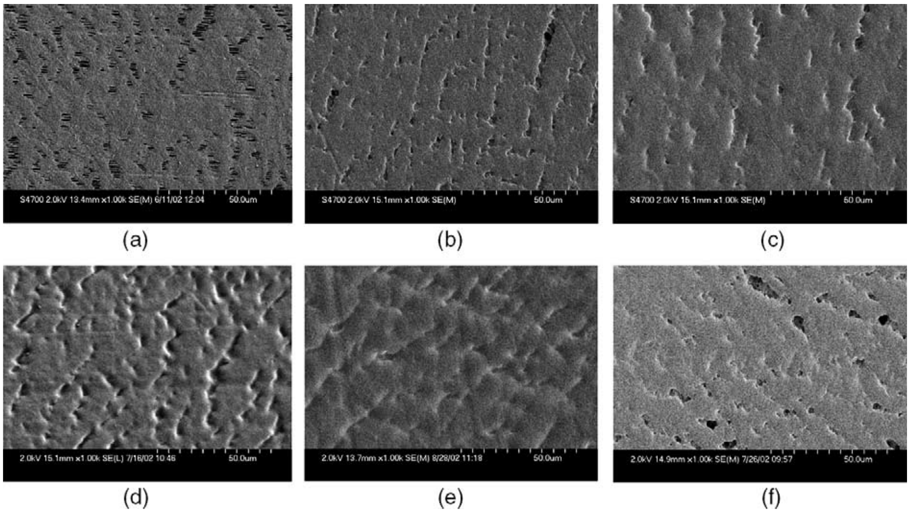

Fig. 7. Effect of grafting temperature on the surface morphology of e-PTFE-g-AAm composite membrane (a) pristine e-PTFE; (b) 50 °C grafted; (c) 60 °C grafted; (d) 70 °C grafted; (e) 80 °C grafted; (f) 85 °C grafted.

3.4. Degree of grafting effect on vapor permeation performance

The degree of grafting effect on the permeation rate and water content in the permeate for vapor permeation of 90 wt.% EtOH aqueous solution through e-PTFE-g-AAm membranes is shown in Fig. 9. The permeation rate increases as the degree of grafting increases. This phenomenon might be due to increased surface hydrophilicity when the degree of grafting increases (Table 3). e-PTFE-g-AAm membrane hydrophilicity was evidenced from the water contact angle experiments. A larger contact angle indicates less hydrophilicity, suggesting that less AAm is grafted. Table 3 shows that the

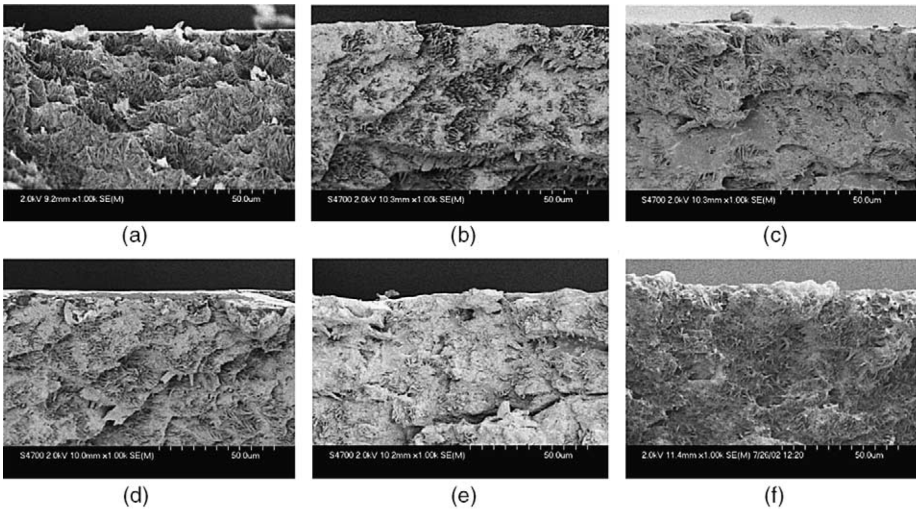

Fig. 8. Effect of grafting temperature on the cross-section morphology of e-PTFE-g-AAm composite membrane (a) pristine e-PTFE; (b) 50 °C grafted; (c) 60 °C grafted; (d) 70 °C grafted; (e) 80 °C grafted; (f) 85 °C grafted.

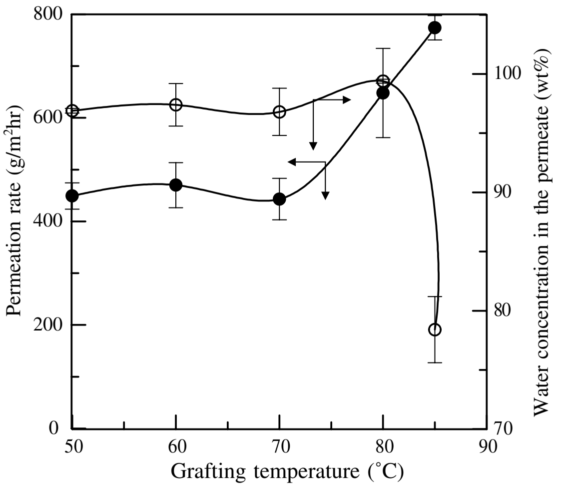

Fig. 9. Effect of grafting temperature on the vapor permeation performances by e-PTFE-g-AAm composite membranes.

Table 3
Surface contact angle with water of pristine and e-PTFE-g-AAm composite membranes by different grafting temperatures

Membranes	Surface contact angel with water (°)
Pristine e-PTFE	109.7
O_2 plasma treated e-PTFE	91.5
50 °C grafted	65.5
60 °C grafted	43.3
70 °C grafted	42.3
80 °C grafted	34.1
85 °C grafted	63.2

contact angle of the pristine e-PTFE membrane was 109.7°, which is higher than that for the e-PTFE-g-AAm membranes. This result confirms that the hydrophilicity increases as more AAm monomers are grafted onto the e-PTFE membrane surface. The hydrogen-bonding interaction between the e-PTFE-g-AAm membrane and the water molecules in the feed solution is stronger than that between the pristine e-PTFE membrane and water. This results in higher water permselectivity for the e-PTFE-g-AAm membrane. However, the water concentration in the permeate decreases sharply for the e-PTFE-g-AAm membrane grafted at 85 °C. This might be due to the lower degree of grafting and the grafting efficiency (Figs. 3 and 4) obtained at 85 °C polymerization temperature. The optimum vapor permeation performance was obtained by an e-PTFE-g-AAm membrane with a 21% degree of grafting for a 90 wt.% aqueous ethanol solution, producing a water concentration in the permeate of 99.4% and a permeation rate of 648 g/m^2 h.

3.5. Feed composition effect on vapor permeation performance

The ethanol concentration effect of the feed mixture on the vapor permeation performance of the e-PTFE-g-AAm membrane is shown in Fig. 10. The vapor permeation experiment was carried out as follows: The feed solution was vaporized first, and then permeated through the e-PTFE-g-AAm membrane. The side of the e-PTFE faced the feed mixture vapor and the grafted layer faced the vacuum system. The permeation rate and separation factor increased with increasing the ethanol

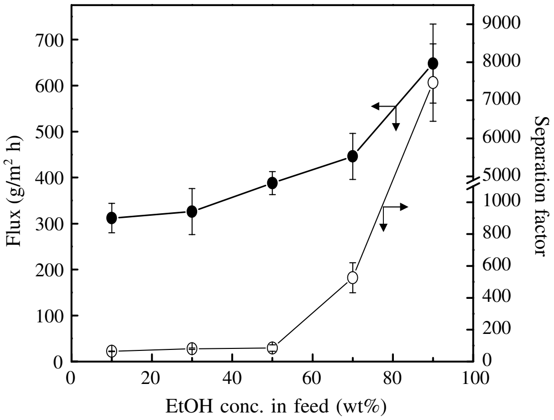

Fig. 10. Effect of feed concentration on the performances of e-PTFE-g-AAm composite membrane (80 °C grafted).

concentration in the feed mixtures. This result can be explained by the plasticizing effect of ethanol. Generally, the hydrophobic membrane has a stronger interaction with alcohol than with water. When the ethanol concentration in the feed is higher, the amorphous region of the membrane is swollen to a larger degree. Hence, the polymer chain becomes more flexible and decreases the energy required for the permeant to diffuse through the membrane. This results in a higher permeation rate. In addition, the higher e-PTFE membrane affinity for ethanol can be further illustrated by considering the differences in the solubility parameters. The solubility parameter difference between ethanol and e-PTFE membrane ($\delta_{\text{e-PTFE}} - \delta_{\text{EtOH}} = 5.4$ (cal/cm^3)$^{1/2}$) is lower than that between water and the e-PTFE membrane ($\delta_{\text{e-PTFE}} - \delta_{H_2O} = 16.1$ (cal/cm^3)$^{1/2}$). That is, ethanol has a stronger interaction with e-PTFE than water, resulting in the membrane becoming swollen from the higher ethanol concentration in the feed solution. Once the water molecules are incorporated into the e-PTFE-g-AAm membrane, they can easily diffuse through the e-PTFE-g-AAm membrane because the interaction between the water molecules and the e-PTFE-g-AAm membrane is very week and the molecular size of water is smaller than that of ethanol. Thus, higher ethanol content results in an increased separation factor.

3.6. Vapor permeation properties of the e-PTFE-g-AAm membrane for different aqueous alcohol mixtures

The alcohol mixture effect on the vapor permeation performance of e-PTFE-g-AAm membranes with a 21% degree of grafting for a 90 wt.% aqueous alcohol solution is shown in Table 4. It shows that an increase in the number of carbon atoms in the alcohol results in an increase in the water concentration in the permeate. However, a decrease in the permeation rate occurs for vapor permeation. These results can be explained by the molecular size and shape of the alcohol: the molecular length L (Å) of methanol, ethanol, and *n*-propanol are 2.9, 4.2, and 5.4, respectively. The water concentration in the permeate was found to depend on the molecular length for this linear alcohol series. The interaction between the permeants and polymer membranes can be used to further explain the above phenomena. The difference in the solubility parameters between the polymer membrane and the different alcohols are summarized in Table 5. The difference in solubility parameters between the polymer membrane and the alcohols follows the order of methanol > ethanol > *n*-propanol. That is, the larger the alcohol molecule, the higher the affinity for the membrane. Once the larger-sized alcohol molecules are incorporated into the e-PTFE-g-AAm membrane, it is difficult for them to diffuse through the membrane. It was also found that the permeation rate of iso-propanol was lower than that for *n*-propanol, which might be due to the higher steric hindrance of iso-propanol than *n*-propanol.

Table 4
Effect of alcohol mixtures on the vapor permeation performances of e-PTFE-g-AAm membranes with a 21% degree of grafting for a 90 wt.% aqueous alcohol solution

Alcohol solution (90 wt.%)	Permeation rate (g/m^2 h)	H_2O in permeate (wt.%)
Methanol	699	67.8
Ethanol	648	99.4
n-Propanol	427	99.5
Iso-propanol	400	99.5

Table 5
Solubility parameter differences between the e-PTFE membrane and alcohols

Permeating molecular	δ (cal/cm^3)$^{1/2}$	$\delta_{\text{e-PTFE}} - \delta_{\text{alcohol}}$
Water	23.4	16.1
Methanol	14.5	7.2
Ethanol	12.7	5.4
n-Propanol	11.9	4.6
Iso-propanol	11.5	4.2

4. Conclusion

In this investigation, the plasma-induced polymerization technique was used to improve the membrane morphology and vapor permeation performance of e-PTFE membranes. The degree of grafting and surface hydrophilicity was increased by increasing the polymerization temperature. A maximum value was obtained at 80 °C. The water contact angle of the pristine e-PTFE membrane and the e-PTFE-g-AAm membrane with a 21% degree of grafting were 109.7° and 34.1°, respectively. The membrane surface roughness increased after plasma treatment and was decreased by grafting a homogenous AAm polymer layer. The optimum vapor permeation performance was obtained using an e-PTFE-g-AAm membrane with a 21% degree of grafting for a 90 wt.% aqueous ethanol solution. This membrane produced a water concentration in the permeate of 99.4% and a permeation rate of 648 g/m^2 h.

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