Plasma-Induced Solid-State Polymerization Modified Poly(tetrafluoroethylene) Membrane for Pervaporation Separation of Aqueous Alcohol Mixtures

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ABSTRACT: Acrylamide (AAm) solid state polymerization was induced using argon plasma to improve the pervaporation performance of poly(tetrafluoroethylene) (PTFE) membranes (PTFE-*g*-PAAm) in aqueous alcohol mixtures. The surface morphology, chemical composition, and hydrophilicity changes in the PTFE and PTFE-*g*-PAAm membranes were investigated using ATR-FTIR, SEM, AFM, X-ray photoelectron spectroscopy, and water contact angle measurements. The surface hydrophilicity rapidly increased with increasing Ar exposure time, but decreased after longer Ar exposure time because of the degradation in the PTFE-*g*-PAAm membrane grafted layer. Compared with the hydrophilicity of the pristine PTFE membrane (water contact angle = 120°), the argon plasma induced acrylamide (AAm) solid-state polymerization onto the PTFE surface (water contact angle = 43.3°) and effectively improved the hydrophilicity of the PTFE membrane. This value increases slowly with increasing aging time and then reaches a plateau value of about 50° after 10 days of storage under air. The pervaporation separation performances of the PTFE-*g*-PAAm membranes were higher than that of the pristine PTFE membrane. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 909–919, 2006

Key words: poly(tetrafluoroethylene); plasma; solid-state polymerization; pervaporation

INTRODUCTION

Binary liquid mixture separation has received increasing attention. The pervaporation process uses a membrane to separate liquid mixtures. This is a promising membrane separation process for azeotropic mixtures, heat-sensitive mixtures, mixtures having nearly the same boiling point, isomers, and the removal of volatile organic compounds from wastewater because of its potential energy cost savings.[1–5] The pervaporation process involves three steps: (1) selective sorption into the membrane on the feed side, (2) selective diffusion through the membrane, and (3) desorption into a vapor phase on the permeate side. However, the desorption step hardly contributes to the transport resistance. The transport mechanism can be described using the solution-diffusion model, $P_i = D_i S_i$. According to this model, solubility (S) and diffusivity (D) enhancement are necessary for the permeation (P) of the fast component, and reduction for the slow component is required to improve the pervaporation separation performance. Generally, small molecules diffuse more easily through a dense membrane. The solubility of a species in a polymer is governed by the chemical affinity between the penetrant and the membrane. Thus, many researchers focused their attention on improving penetrant solubility in the membrane, including plasma grafting, polymer blend, chemical grafting, and preparing new polymers.[6–9]

Poly(tetrafluoroethylene) (PTFE) is an attractive material for pervaporation because of its outstanding properties, high chemical inertness, thermal stability, and mechanical strength. The hydrophobic surface of PTFE membrane produces a low water permeation rate and selectivity for pervaporation dehydration separation process. Therefore, pretreatment on PTFE surface is required to achieve satisfactory hydrophilicity to improve the separation performance. There have been many studies on improving the surface properties of PTFE using various surface modification methods, such as chemical etching with sodium naphthalene,[10] UV-lasers, electron and ion beams irradiation,[11,12] and plasma modification.[13–16] All of these methods lead to large increases in the surface energy and surface hydrophilicity. Among these methods, plasma modification is the most notable technique. Plasma treatment is a useful technique for polymer surface modification. After plasma treat-

ment, the hydrophobic polymer surface becomes a hydrophilic surface. However, the hydrophilicity of the plasma-modified surface is unstable. Many works have found that the water contact angle of the plasma modified membrane surface increases with increasing aging time. This phenomenon is called hydrophobic recovery (the aging effect).[17] This is unfavorable for many technological applications. This phenomenon is due to the migration of hydrophilic groups formed by the plasma activation from the surface layer into the bulk layer because of the thermal motion of polymer chains.[17,18] The aging effect can be suppressed if we can restrain the polymer chain migration. There are various ways to restrain polymer chain migration. One method is storing the plasma modified polymer film in hydrophilic or low temperature (below T_g) atmosphere.[19] Another way is to introduce longer hydrophilic polymer chains onto the polymer surface. The larger hydrophilic polymer chains would have difficulty migrating into the bulk layer. The modified polymer surface will therefore remain hydrophilic.

Plasma-induced postgrafting copolymerization reaction can graft long hydrophilic polymer chains onto the hydrophobic polymer backbone. However, the plasma-induced postgrafting reaction involves many complex steps: (1) surface activation by plasma to produce free radicals, (2) activated polymer immersion into a monomer solution in vacuum, and (3) rinsing off the residual homopolymer. This complex process is difficult to commercialize. The other knotty problem is that the relatively high grafting degrees lead to a grafted polymer layer blocking the membrane pores.[20] Plasma-induced solid-state polymerization is a simple process for grafting long hydrophilic polymer chains onto the hydrophobic polymer surface. Solid-state polymerization is usually induced by heating, UV, or γ-ray irradiation. Plasma is a mixture of electrons, ions, radicals, and UV that is able to initiate chemical reactions against the polymer surface and induce polymerization. Kou et al. grafted hydrophilic polymer chains onto a polypropylene membrane surface using plasma to induce the solid-state polymerization of α-allyl glucoside to improve the antifouling property.[21] However, there is no literature investigating

how to apply this technique to a PTFE surface to improve the hydrophilicity and restrain the hydrophobic recovery phenomenon on a modified PTFE membrane surface.

The objective of this study was to investigate how plasma is used to induce solid-state polymerization to modify a hydrophobic PTFE surface for the pervaporation separation process, and suppress the surface hydrophobic recovery effect.

EXPERIMENTAL

Materials

The PTFE membrane was received from Nitto Denko (Nitofuron no. 900UL) as 350 mm wide and 80 μm thick. Specimens were cut to a dimension of 50×50 mm^2 and used for the surface modification experiments. Prior to the plasma treatment, the membranes were washed with acetone in an ultrasonic washer and dried at room temperature under vacuum. Acrylamide, *N*-methylolacrylamide, and *N*-isopropylacrylamide were used as the monomers for graft polymerization without further purification. Methanol, ethanol, and ethanol/acetone (50/50, v/v) mixture were used as the solvent of monomer without further purification. The hydrogen and argon used for plasma irradiation were of pure grade (purity, 99.995%).

Plasma-induced graft polymerization

The plasma-induced graft polymerization of acrylamide, *N*-methylolacrylamide, and *N*-isopropylacrylamide onto the PTFE membrane surface was carried out in three steps: (1) peroxide formation onto the PTFE surface by hydrogen plasma irradiation, (2) hydrophilic monomer solution sprayed onto the hydrogen plasma activated PTFE surface, and (3) hydrophilic monomer graft polymerization from the peroxides using argon plasma exposure. The graft polymerization process is illustrated in Figure 1. The apparatus used for the hydrogen plasma activation and argon plasma-induced grafting reaction is a glass cylinder reactor externally equipped with capacity coupling electrodes (Samco International, Kyoto, Japan; model RFG-
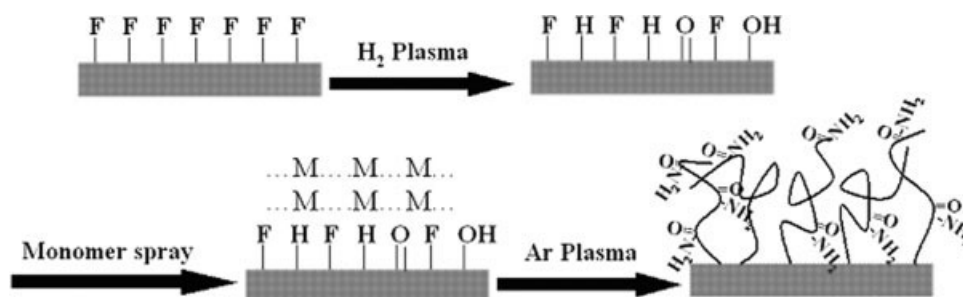

Figure 1 Schematic description of grafting of hydrophilic monomer onto PTFE membrane by plasma-induced polymerization process.

TABLE I
Contact Angle of Different Solvents on PTFE Membrane Surface

Solvent	Contact angle (°)
H_2O	119.1
Methanol	55.1
Ethanol	40.9
Acetone	33.2
Ethanol/acetone (50/50, v/v) mixture	35.7

TABLE III
Degree of Swelling of PTFE Membrane by Different Solvents

Solvent	Degree of swelling (%)
H_2O	0.11 ± 0.02
Methanol	0.23 ± 0.04
Ethanol	0.32 ± 0.06
Acetone	0.43 ± 0.04
Ethanol/acetone (50/50, v/v) mixture	0.39 ± 0.05

300). The reactor contained a micrometer valve for hydrogen and argon gas inlet, a pressure gauge, and a vacuum system composed of a combination of diffusion and rotary pumps. The plasma was ignited at a radio frequency of 13.56 MHz, 50 W, and a pressure of 0.1 Torr. The PTFE membrane surface was activated for 60 s with hydrogen plasma to form carbon radicals on the PTFE surface. The specimen was subsequently exposed to air to form peroxides that were able to initiate the graft polymerization. After the hydrogen plasma activated PTFE surface was sprayed with a 3–15 wt % monomer solution, it was dried at 30°C in an oven. The PTFE membrane surface coated with monomer was irradiated by argon plasma with an exposure time of 60–240 s to induce the graft copolymerization reaction. After graft polymerization, the PTFE membrane was washed with water using an ultrasonic washer, to remove the excess homopolymer, and dried at 30°C in an oven.

Water contact angle measurement

The surface wettability of pristine and plasma-modified membranes were characterized by the surface contact angle of water. The contact angles of water on the plasma-modified PTFE membrane surfaces were measured using the sessile drop method.[2] The measurement was carried out at room temperature with a goniometer (Erma, Tokyo, Japan; model G-1). The aged in air plasma-treated (PTFE) membrane water contact angles were measured based on increasing storage time. Aged PTFE membranes were stored in 1 atm pressure and 25°C. The water contact angle was measured to observe the hydrophilic recovery of plasma-treated PTFE membranes. The contact angle was determined from an average of 10 measurements.

TABLE II
Solubility of Acrylamide in Various Solvents at 30°C

Solvent	Solubility (g/100 mL solvent)
Water	215.5
Methanol	155
Ethanol	86.2
Acetone	63.1
Ethanol/acetone (50/50, v/v) mixture	71.2

Attenuated total refraction–Fourier transform infrared spectra of the plasma-modified PTFE membrane

Attenuated total refraction–Fourier transform infrared (ATR-FTIR) spectra for the plasma-modified PTFE membrane surfaces were obtained using the PerkinElmer spectrophotometer equipped with a multiple internal reflectance apparatus. A ZnSe prism was used as an internal reflection element. Wave ranges from 4000 to 650 cm^{-1} were scanned 16 times for spectrum integration.

Surface morphology observation by scanning electron microscopy

Before and after plasma treatment, the specimen was coated with Au. The surface morphology of the plasma-modified PTFE membranes were observed using scanning electron microscopy (SEM) (Hitachi Co.) with the accelerating voltage set to 15 kV.

Surface topology observation by atomic force microscopy

The topographic measurements of untreated PTFE membranes, hydrogen plasma treated PTFE membranes, and AAm-grafted PTFE membranes were examined using an atomic force microscopy (AFM)
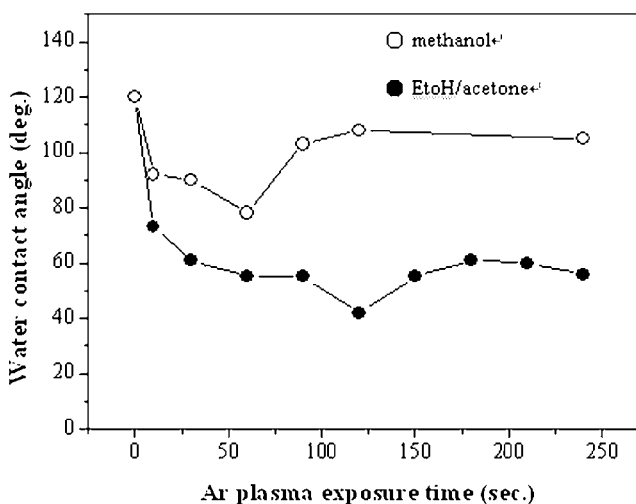

Figure 2 Effect of plasma treatment time on the hydrophilicity of PTFE-*g*-PAAm membrane (AAm conc., 15 wt %).
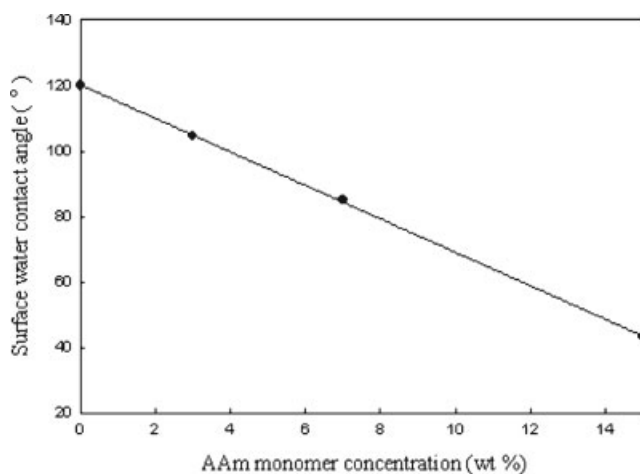
Figure 3 Effect of AAm monomer concentration on the surface water contact angle of PTFE-*g*-PAAm membrane (Ar plasma exposure time, 120 s).

(Digital Instrument, DI 5000) in the tapping mode to observe their surface configurations. An area of 3 × 3 nm^2 was scanned. The surface arithmetic average roughness (R_a), root-mean-square roughness (R_{ms}), and the maximum roughness (R_{max}) of the modified PTFE membranes were calculated from the images obtained from the AFM. The values of roughness were defined from the following equations[22]:

$$R_a = \frac{1}{L_x L_y} \int_{Y_T}^{Y_B} \int_{X_L}^{X_R} \left| Z_i - Z_0 \, dx \, dy \right| \qquad (1)$$

$$R_{ms} = \sqrt{\frac{1}{L_x L_y} \int_{Y_T}^{Y_B} \int_{X_L}^{X_R} (Z_i - Z_0)^2 \, dx \, dy} \qquad (2)$$

$$R_{max} = Z_{max} - Z_{min} \qquad (3)$$

X-ray photoelectron spectra

X-ray photoelectron spectra (XPS) analysis of the pristine and plasma-modified PTFE membranes were obtained using a Shimadzu ESCA 3400 equipped with an Mg K$_\alpha$ photo source. The anode voltage was 6 kV, the anode current was 20 mA, and the background pressure in the analytical chamber was 1.0 × 10^{-5} Pa. The diameter of the X-ray spot was 6 mm, and the take-off angle of the photoelectrons was 70° with respect to the sample surface. The XPS spectra were referenced to the 690.0 eV F$_{1s}$ level, observed to eliminate the charge effect. The C$_{1s}$ and N$_{1s}$ spectra were decomposed by fitting a Gaussian–Lorentzian mixture function (the mixture rate was 60:40).

Pervaporation experiment

A traditional pervaporation process was used.[2] The feed solution was in direct contact with the

membrane and kept at 25°C. The effective area was 7.07 cm^2. In this experiment the permeation rate was measured using the permeant weight. The feed solution and permeate compositions were measured using gas chromatography (G.C. China chromatography 8700T).

RESULTS AND DISCUSSION

Solvent and monomer effect on the PTFE membrane surface contact angles

Coating a uniform monomer layer onto the substrate surface was very important in the plasma-induced solid-state polymerization process. One must choose a monomer that has good affinity with the PTFE surface and can dissolve into it. Surface contact angle measurement is a simple way to determine the affinity between various solvents and the PTFE membrane surface. Tables I and II show the surface contact angle of a series of solvents on PTFE membranes and the solubility of the acrylamide in these solvents. Table II shows that the acrylamide solubility in various solvents ranked in the following order: water > methanol > ethanol > acetone. However, an opposite trend for the affinity between the solvents and PTFE membranes was observed, as shown in Table I. Even though the highest acrylamide solubility occurs in water, it is difficult to spray the aqueous acrylamide monomer solution onto the PTFE membrane surface because of the lower wettability of water with PTFE, as evident from the surface contact angle results shown in Table I. Compared with the surface contact angle results (Table I), the solvent effect on the degree of PTFE membrane swelling (Table III) exhibited a similar
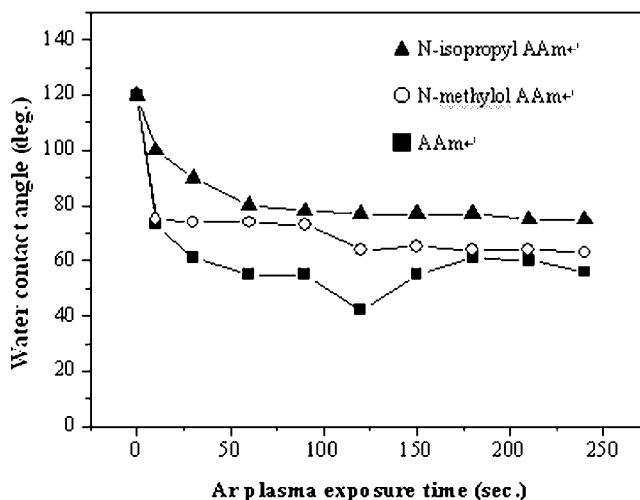

Figure 4 Effect of different monomers on the surface water contact angle of Ar plasma grafted PTFE membrane (monomer conc., 15 wt %).
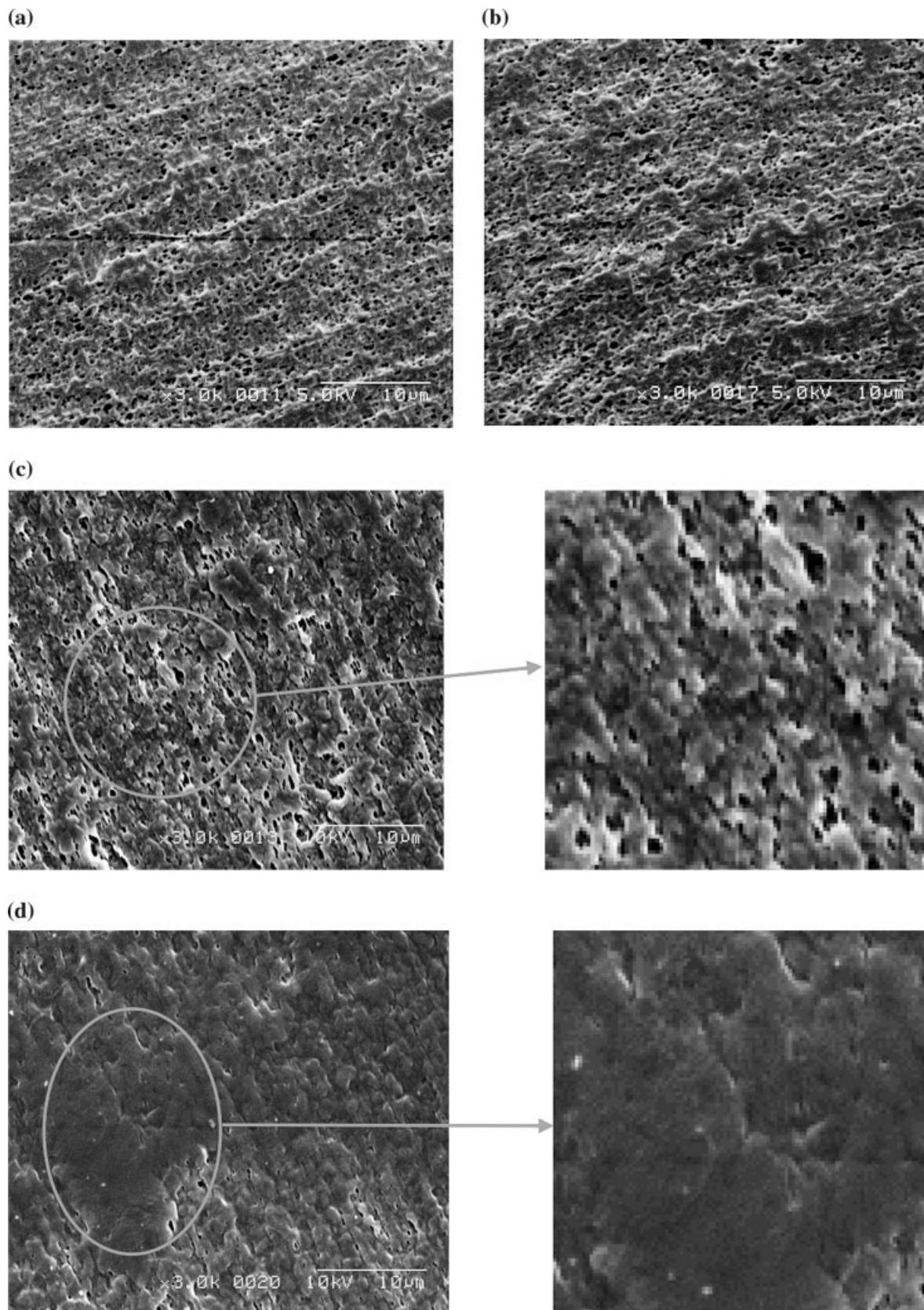
Figure 5 SEM micrographs of PTFE membrane: (a) Pristine PTFE, (b) H_2 plasma treated, (c) Ar plasma grafted AAm/MeOH, and (d) Ar plasma grafted AAm/acetone–EtOH mixture.

trend. Thus, the ethanol/acetone (50/50, v/v) mixture was chosen as the AAm monomer solvent because the optimum monomer solubility and surface wettability on the PTFE membrane could be obtained with this mixed solvent.

Plasma treatment condition effect on the surface water contact angle of grafted PTFE membranes

Figure 2 shows the plasma treatment time effect on the hydrophilicity of the PTFE-g-PAAm membrane. From this figure it is observed that with increasing Ar exposure time the surface water contact angle decreased rapidly, passed through a minimum, and then increased gradually. The initial decrease in the water contact angle with increasing Ar exposure time may be ascribed to the increase in acrylamide grafting onto the PTFE surface. However, at higher Ar exposure time (after 50 s) the water contact angle decreases, signifying a decrease in grafting, which may be due to acrylamide layer etching from the membrane surface by various energetic species present in the plasma. From Figure 2 it is also observed that for the same Ar exposure time ethanol/acetone mixed solvent system shows a higher amount of grafting than does methanol. This is because of better uniformity of acrylamide layer on PTFE membrane surface by the mixed solvent as evident from the contact angle measurement result given in Table I. In addition, the AAm monomer concentration effect on the surface contact angle of the PTFE-g-PAAm membrane (Ar plasma exposure time, 120 s) is shown in Figure 3. It shows that the surface water contact angle decreases with increasing monomer concentration. This might be due to the monomer concentration increase, resulting in an increase in the degree of grafting. Acrylamide, N-methylolacrylamide, and N-isopropylacrylamide were used as monomers for graft copolymerization with PTFE to investigate the effect of different monomer substitution groups on the modified PTFE membrane surface hydrophobicity, as shown in Figure 4. It shows that the hydrophilicity of the PTFE-g-PAAm membrane is higher than that of the N-methylolacrylamide and N-isopropylacrylamide grafted PTFE membranes. These phenomena might be due to the increase in steric hindrance from the vinyl monomer with bulk pendent group (N-methylolacrylamide and N-isopropylacrylamide), resulting in a decrease in the degree of grafting.

Surface topography of the PTFE-g-PAAm membrane

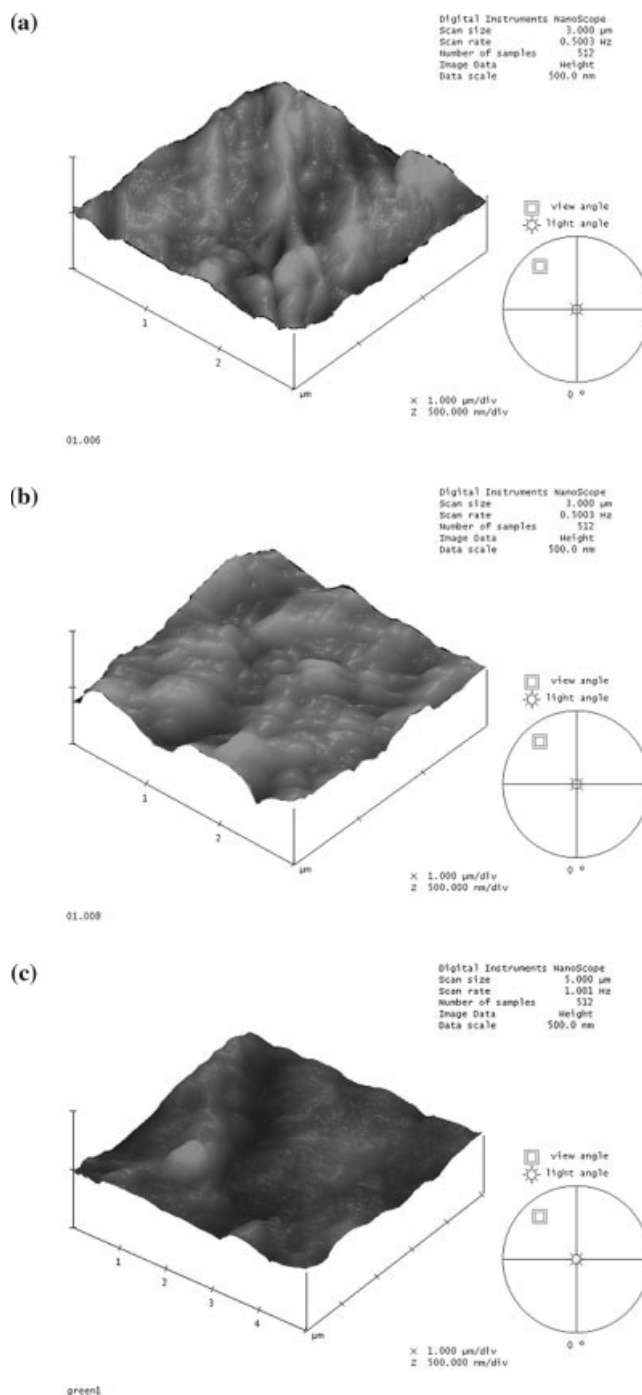To evaluate the plasma-induced solid-state polymerization effect on the PTFE-g-PAAm membrane sur-

Figure 6 The AFM image of PTFE membrane surface after plasma treatment and grafted acrylamide: (a) Pristine PTFE, (b) H$_2$ plasma treatment for 1 min, and (c) PTFE-g-PAAm membrane.

face structures, the results were further confirmed by SEM analysis. SEM micrographs of the pristine PTFE membrane and PTFE-g-PAAm membranes at different plasma conditions were taken (Fig. 5). To make the hydrophilic monomer efficiently coat onto the PTFE surface, the PTFE membrane was first

TABLE IV
Surface Roughness Values of the Pristine, H₂ Plasma Treated PTFE, and PTFE-*g*-PAAm Membranes

Membrane	R_{ms}[a] (nm)	R_a[b] (nm)	R_{max}[c] (nm)
Pristine PTFE	29.908	24.045	198.81
H₂ plasma treated PTFE	43.741	34.206	352.03
PTFE-*g*-PAAm[d]	40.503	31.916	310.49

[a] Root mean square (RMS) of z values.
[b] Arithmetic average roughness.
[c] Mean difference between the five highest peaks and the five lowest values.
[d] Grafting amount of the PTFE-*g*-PAAm membrane, 458 mg/m² (AAm conc., 15 wt %; Ar plasma exposure time, 120 s).

treated with hydrogen plasma. The PTFE surface treated with H₂ plasma [Fig. 5(b)] seems similar to the pristine PTFE membrane. Compared with the pristine PTFE membrane [Fig. 5(a)], the surface pore size of the PTFE-*g*-PAAm membrane [Figs. 5(c) and 5(d)] reduced slightly. This phenomenon might be because the hydrophilic layer of PAAm was successfully grafted onto the PTFE membrane surface. That the mixed solvent system confers better grafting uniformity than does methanol is also evident from their surface morphologies, as shown in Figures 5(c) and 5(d) for mixed solvents and methanol, respectively. The plasma modification process influence on the surface roughness of the PTFE membranes was also investigated using AFM. The surface AFM micrographs and roughness values are shown in Figure 6 and Table IV respectively. It could be seen that the PTFE membrane surface roughness was changed by the plasma treatment. The

surface roughness of direct H₂ plasma treated PTFE was higher than that of the pristine PTFE membrane. This result indicated that direct H₂ plasma treatment produces an etching effect on PTFE. However, the surface roughness of the PTFE-*g*-PAAm membrane was somewhat lower than that of the H₂ plasma treated PTFE membrane. This might be because the grafted AAm layer on the membrane surface caused the membrane to become smoother.

Chemical composition of the PTFE-g-PAAm membrane surface

Figure 7 shows the ATR/FTIR spectra of the (a) acrylamide monomer, (b) acrylamide dissolved in ethanol/acetone (50/50, v/v) mixture and dried on the glass plate, (c) pristine PTFE, and (d) PTFE-*g*-AAm membrane. In the ATR/FTIR spectra for the acrylamide monomer, absorption peaks appear at 984, 839, and 815 cm⁻¹, which correspond to the alkene CH vibrations of vinyl amides. The spectra of the acrylamide that dissolved in ethanol/acetone (50/50, v/v) mixture solution were the same as those of the acrylamide monomer. The AAm monomer did not polymerize, and so the AAm structure was the same before and after dissolving in the solvent. However, in the FTIR spectra of the pristine PTFE membrane, strong absorption peaks appear at 1204 and 1149 cm⁻¹ only, which correspond to the fluorine-containing compound (CF_2, CF_3) in PTFE. The PTFE-*g*-AAm membrane surface spectrum showed a new absorption peak at 1661 cm⁻¹, which was not found in the FTIR spectrum of the pristine PTFE membrane,
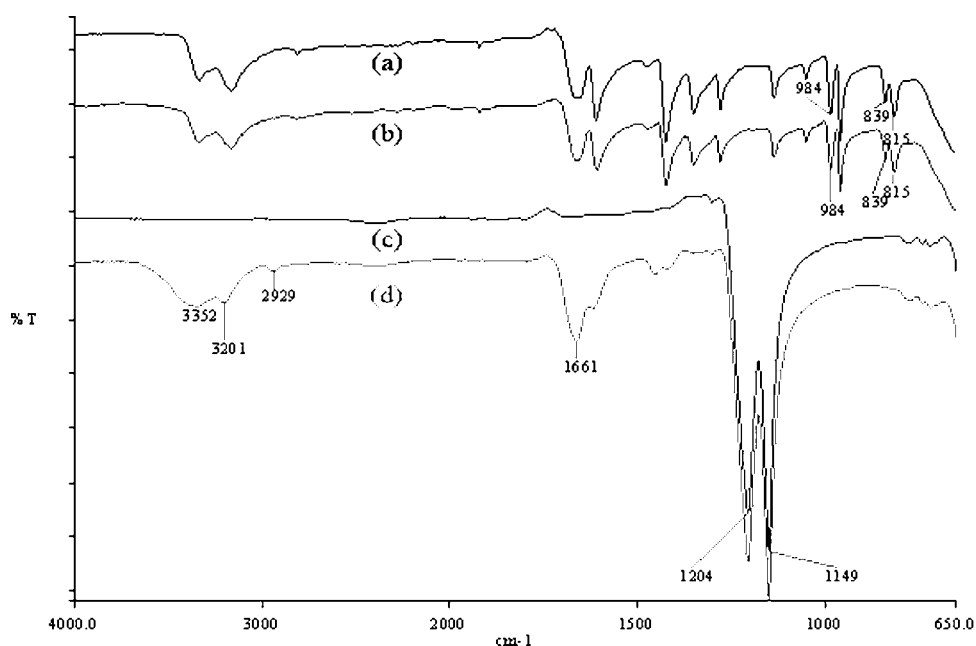

Figure 7 ATR/FTIR spectra of the (a) acrylamide monomer, (b) acrylamide dissolved in ethanol/acetone (50/50, v/v) mixture and dried on the glass plate, (c) pristine PTFE, and (d) PTFE-*g*-PAAm membrane.
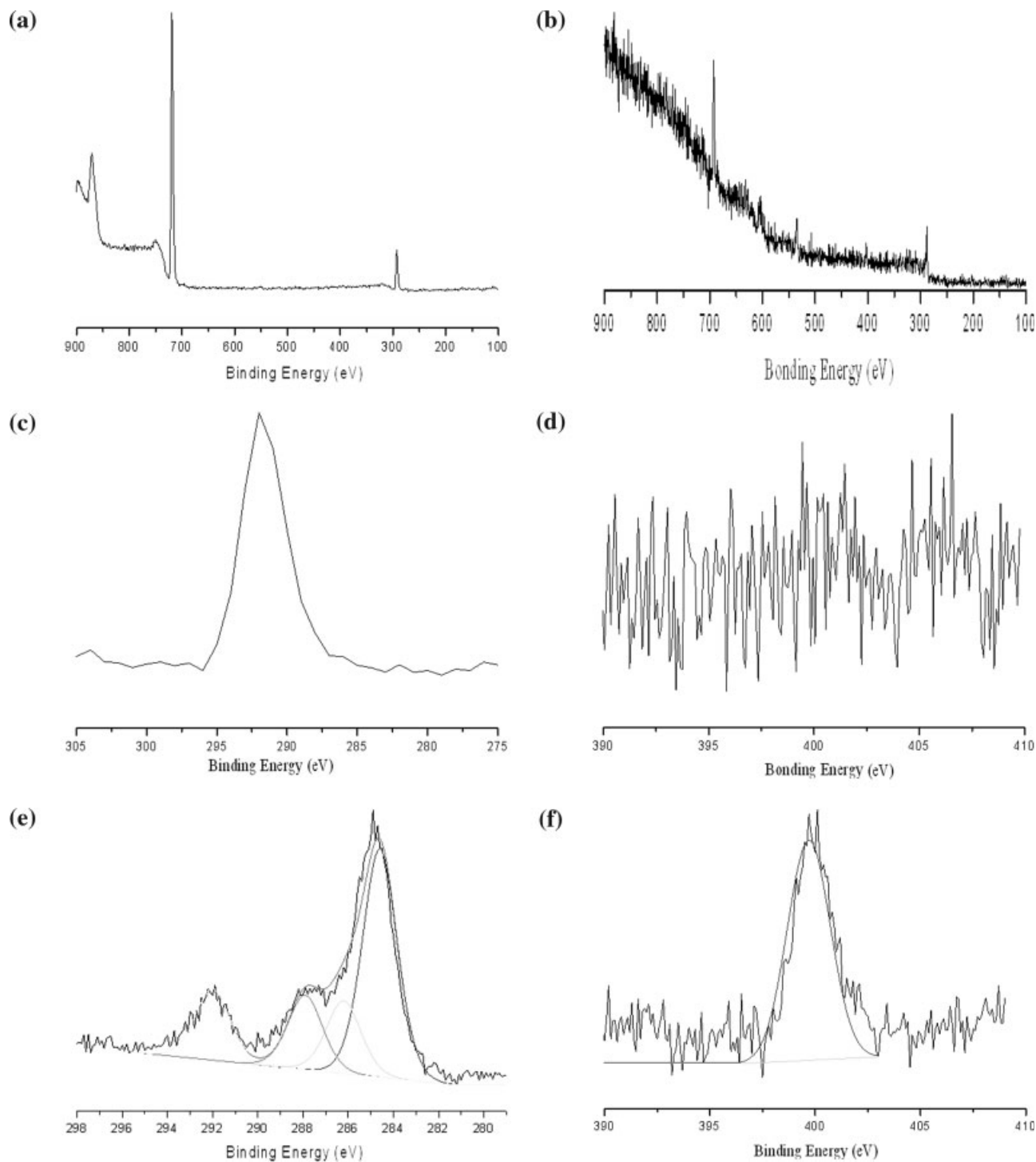
Figure 8 XPS wide scan of (a) untreated PTFE membrane and (b) 15 wt % PTFE-*g*-PAAm membrane; C_{1s} core-level XPS spectra of (c) untreated PTFE membrane and (e) 15 wt % PTFE-*g*-PAAm membrane; N_{1s} core-level XPS spectra of (d) untreated PTFE membrane and (f) 15 wt % PTFE-*g*-PAAm membrane.

ascribed to the carbonyl group of primary aliphatic amides. It clearly characterizes the grafting, since during polymerization the double bond (vinyl) is converted to single bond through bonding with PTFE surface. These results provide evidence to successful grafting of AAm onto the PTFE membrane

surface. The chemical composition on the pristine PTFE and PTFE-*g*-PAAm surface was analyzed with XPS. Figure 8 shows the wide scan, and C_{1s} and N_{1s} narrow scan spectra of the PTFE and 15 wt % AAm grafted PTFE-*g*-PAAm membranes. The pristine PTFE surface presented 291.4 eV for C—F and a lit-

TABLE V
Chemical Composition of PTFE-g-PAAm Membranes by Different Ar Plasma Exposure Time

Ar plasma exposure time (s)	Grafting amount (mg/m²)	Atomic composition on the PTFE-g-PAAm surfaces		
		F/C atom ratio	O/C atom ratio	N/C atom ratio
0	0	2	0.02	0.00
60	354	0.38	0.25	0.04
120	458	0.39	0.23	0.11
240	319	0.3	0.13	0.03

tle amount of C—C appeared in 284.6 eV. The presence of surface-grafted AAm can be deduced from the C_{1s} core-level spectra associated with the functional grafted polymer group, with the peak components centered at ~284.6 eV for the CH species, 286.2 eV for the C—O species, 287.9 eV for the $CONH_2$.[23] The PTFE membrane surface also showed no N_{1s} spectra. However, the AAm-grafted PTFE membrane contained a N_{1s} core level component at 399.7 eV due to the NH structure of the grafted AAm polymer. These results confirmed that the AAm monomer was grafted onto the PTFE surface through the Ar plasma induced acrylamide solid-state polymerization procedure. The atomic compositions for the PTFE-g-PAAm surfaces using different Ar plasma exposure times were estimated from the relative intensities of C_{1s}, F_{1s}, O_{1s}, and N_{1s} core-level spectra. Table V summarizes the estimation results. From this table it is observed that the F/C, N/C, and O/C ratios for pristine PTFE are 2, 0, and 0.02, respectively, corresponding to the theoretical values based on its chemical structure. The small value of O/C (instead of theoretical 0 value) was due to presence of some oxygen contaminants on PTFE surface. From Table V it is also observed that with increase in Ar plasma exposure time both O/C and N/C ratios increase because of incorporation of oxygen and nitrogen from acrylamide moiety on the PTFE surface through grafting. In a similar way the carbon atom from acrylamide decreases the F/C ratios through grafting. It is also interesting to note that above 120 s Ar exposure time both O/C and N/C ratios decrease because of grafting degradation by etching.

Aging effect on the surface water contact angle of the PTFE-g-PAAm membrane

To investigate the effect of storage time on the surface hydrophilicity of PTFE-g-PAAm membrane, the aging behavior of the modified PTFE membranes during storage in room temperature and air environment were studied. Figure 9 shows the water contact angle variation of the Ar plasma pretreated PTFE

membrane and the PTFE-g-PAAm membrane. It shows that the Ar plasma pretreated process and plasma-induces solid-state polymerization could enhance the hydrophilicity of the PTFE membrane (surface water contact angle for original PTFE = 120°, The Ar plasma pretreated PTFE = 91°, PTFE-g-PAAm membrane = 43.3°). The surface modification efficiency of the plasma-induced solid-state polymerization was higher than that of the plasma pretreated process. The surface hydrophilicity decreased rapidly and leveled-off after 10 days of storage under atmosphere. These phenomena might be due to PTFE membranes modified by plasma causing a reversible conformational transformation. The plasma-modified layer might be submerged to change the surface free energy of polymer stored under air.

Pervaporation separation performance of PTFE-g-PAAm membrane

Pervaporative dehydration of various alcohols and dimethyl formamide were carried out with pristine PTFE and PTFE-g-AAm membranes and the results are shown in Table VI. Permeation rate and permeate water concentration for various alcohols through grafted and pristine PTFE membranes are given in Table VII. From these tables it is observed that permeation rate and permeate water concentration of grafted PTFE membranes are higher than those for the pristine PTFE membrane. This may be explained in terms of increased hydrophilicity of the grafted membranes (as also evidenced by contact angle measurements given in Table I), which causes preferential water permeation through hydrogen bonding and ion dipole interaction. From Table VII it is also observed that among the various alcohols permeation rate increases with decrease in molar vol-
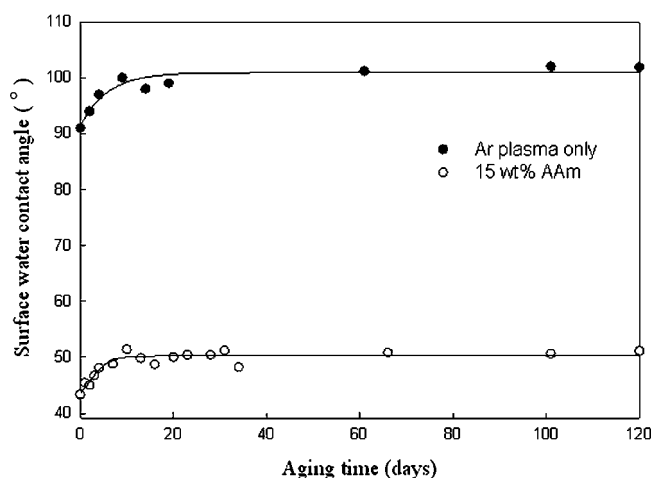

Figure 9 Effect of aging time on the surface water contact angle of Ar plasma treated PTFE and PTFE-g-PAAm membrane.

TABLE VI
Pervaporation Performance of Various Organic Solvent/Water Mixtures for PTFE and PTFE-*g*-PAAm Membranes at 25°C[ab]

Aqueous mixture[b]	Permeation rate (g/m² h)		Water concentration in permeate (wt %)	
	PTFE	PTFE-*g*-PAAm	PTFE	PTFE-*g*-PAAm
90 wt % IPA	285	373	99.7	100
80 wt % TFP	247	310	99.8	99.5
80 wt % DMF	203	239	100	100

IPA, isopropanol; TFP, tetrafluoropropanol; DMF, *N,N*-dimethyl formamide.
[a] Grafting amount of the PTFE-*g*-PAAm membrane, 458 mg/m² (AAm conc., 15 wt %; Ar plasma exposure time, 120 s).
[b] IPA: iso-propanol; TFP: tetrafluoropropanol; DMF: dimethyl formamide.

ume of alcohols from isopropanol to methanol while the reverse trend is observed for water concentration in the permeate. Bigger alcohols diffuse slower than the smaller ones, resulting in their lower permeation and thus higher permeation rate of smaller water molecules through the hydrophilic membranes. The effect of isopropanol (IPA) concentration in feed on permeation rate and permeate water concentration is shown in Figure 10. From this figure it is seen that with the increase in IPA concentration in feed permeation rate decreases linearly while water concentration in permeate remains independent of feed concentration of alcohol.

CONCLUSIONS

PTFE membranes were modified using an Ar plasma induced solid-state polymerization procedure. The solvent and monomer effect, and Ar plasma exposure time on the PTFE membrane surface morphology and pervaporation performance were investigated. The results are summarized as follows:

1. The choice of solvent is an important factor for the grafting process. Mixed solvent sys-

TABLE VII
Effect of Alcohol Mixtures on the Pervaporation Performances of PTFE-*g*-PAAm Membranes for a 90 wt % Aqueous Alcohol Solution at 25°C[a]

Alcohol solution (90 wt %)	Molar volume (mL/mol)	Permeation rate (g/m² h)	H₂O in permeate (wt %)
Methanol	40.7	455	98.9
Ethanol	58.6	437	99.1
n-Propanol	75.1	385	99.5
Isopropanol	76.4	373	100

[a] Grafting amount of the PTFE-*g*-PAAm membrane, 458 mg/m² (AAm conc., 15 wt %; Ar plasma exposure time, 120 s.
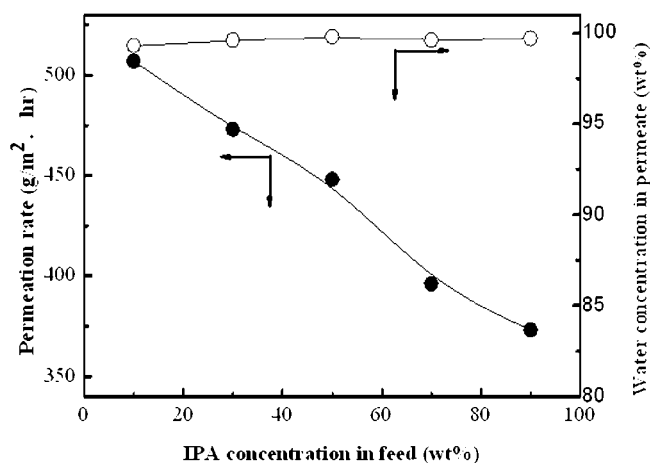

Figure 10 Effect of feed IPA concentrations on the pervaporation performance for PTFE-*g*-PAAm membrane at 25°C.

tems (acetone/ethanol = 50/50) were used in these experiments. The monomer solution could be sprayed onto the PTFE surface very well.
2. The hydrophilicity of the PTFE-*g*-PAAm surface increased with increasing monomer concentration.
3. The hydrophilicity of the PTFE-*g*-PAAm surface increased with increasing Ar plasma exposure time, but decreased after longer exposure time, resulting from the degradation of the grafted layer on the PTFE (etching effect).
4. The surface water contact angle of PTFE-*g*-PAAm increased slowly with increasing aging time and reached a plateau value of about 50° after 10 days of storage under air.
5. The pervaporation performance was obtained using PTFE-*g*-PAAm membranes for a 90 wt % aqueous isopropanol mixture, giving a water concentration in permeate of 100 wt % and a permeation rate of 373 g/m² h.

From these results, it may be concluded that plasma-induced solid-state polymerization is a simple process for effectively modifying PTFE surfaces for pervaporative dehydration.

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