Plasma Graft Polymerization Membrane of Acrylamide for Pervaporation Separation of Aqueous Alcohol Mixtures

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SYNOPSIS

Pervaporation of water–ethanol mixtures through acrylamide-*plasma graft*-polysulfone (AAm-*p*-PSF), a PSF membrane on which AAM is grafted by plasma polymerization, was investigated in this work. The effects of plasma treatment conditions and feed compositions on the pervaporation performances were studied for the un-ionized and ionized AAm-*p*-PSF membranes. It was found that the separation factor of the AAm-*p*-PSF membrane is higher than those of the unmodified membranes. The ionized membrane possesses a separation factor of 10.4 and a permeation rate of 718.1 g/m^2 h. In addition, the surface properties of the prepared membrane were characterized by ESCA, SEM, and a water contact angle meter; and the relationship between the grafting yield and the plasma pretreatment time was obtained. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation is an attractive process for separation of azeotropic mixtures, heat-sensitive mixtures, close boiling point mixtures, and the removal of water from organic liquids.[1–3] It is known that the pervaporation performance can be improved by elevating the hydrophilicity of membranes. Therefore, many research workers attempted to increase the membrane hydrophilicity by using grafting blending, and block copolymerization. In the authors' previous articles several methods, such as [60]Co γ-ray irradiation[4,5] and chemical grafting,[6] were introduced to improve the membrane morphology and the pervaporation performance. In the present work, the plasma graft polymerization technique is used to modify the surface of polysulfone (PSF) membrane for improving its performance in pervaporation. The graft polymerization technique has been widely used to prepare the pervaporation membrane for separation of aqueous alcohol mixtures. Membranes grafted by acrylic acid,[7] methacrylic acid,[8] and butylacrylate[9] have been studied. Acrylamide (AAm), which has high hydrophilicity, is the grafting material discussed in this work. The plasma technique can graft a very thin layer of AAm on the surface of a porous PSF membrane due to the specific surface activation by plasma. Thus the chemical structure of the porous PSF membrane and its properties can be preserved.

The main purpose of this study was to find the optimal plasma treatment conditions for grafting AAm onto the PSF membranes. The effects of plasma treatment conditions and feed compositions on the pervaporation performance of the un-ionized and ionized AAm-*p*-PSF membranes were carefully studied.

EXPERIMENTAL

Materials

PSF (P-1835) was purchased from Amoco Co. Polyvinylpyrrolidone (PVP; K-30) and 2-pyrrolidone were supplied by Janssen Reagent. The solvent used throughout this study was analytical grade *N,N*-dimethylformamide (DMF) from Fisher. The nonwoven fabrics of polyester used as a base in fabrication of PSF membrane were supplied by Hollytex, and the AAm was obtained from Merck Co.
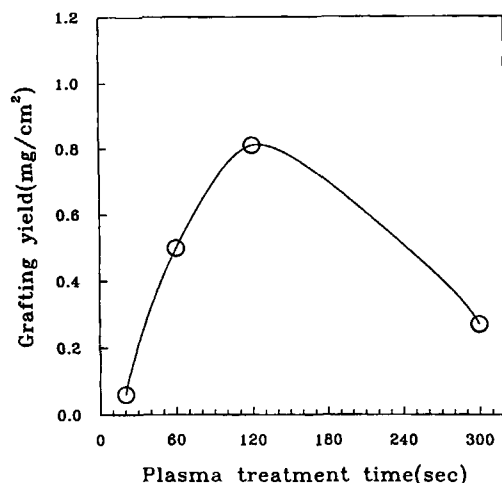
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Figure 1 Effect of plasma treatment time on the grafting yield of acrylamide. Grafting conditions: 10 wt % AAm aqueous solution, 2 h, 60°C, plasma treatment power 10 W.

Preparation of PSF Membrane

The PSF composite membrane was made by a phase inversion process. The dope solution, consisting of 15.2 wt % PSF, 5 wt % PVP, and 3.3 wt % 2-pyrrolidone in DMF, was cast on a glass plate to form a thin film. The glass plate was then immersed in a water gelation bath for 30 min. Afterward the PSF membrane was peeled from the glass and air dried at room temperature.

Plasma Graft Polymerization

A tubular deposition system externally equipped with capacity coupling electrodes (RFG-300, Samco Ltd., Japan) was used in this study.[10] The membrane was placed in the center between two electrodes that were 10 cm apart. The plasma was ignited at a frequency of 13.56 MHz with a power of 10 W for 20–300 s. The tube reactor was evacuated to 0.02 torr. After the membrane was treated by plasma, the degassing aqueous AAm solution (10%) was introduced in the tubular reactor to carry out graft polymerization. The tubular reactor was then put in a reciprocating shaker at 60°C for 2 h. Distilled water was used to wash off the homopolymer for 24 h. Afterward the grafted membrane was dried at room temperature for 24 h and kept in air at 25°C with a relative humidity of 60%.

Ionization of the AAm-p-PSF membrane was accomplished by treating the membrane with 2N NaOH at 60°C for 2 h.[11,12]

Pervaporation Experiments

A traditional pervaporation apparatus was used in this study.[13] The effective membrane area was 10.2 cm[2]. Most of the experiments were conducted at 25°C. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions, permeates, and solutions adsorbed in the membrane were measured by gas chromatography (GC, China Chromatography, 8700T). The separation factor, $\alpha_{H_2O/EtOH}$ was calculated from:

$$\alpha_{H_2O/EtOH} = (Y_{H_2O}/Y_{EtOH})/(X_{H_2O}/X_{EtOH})$$

where X_{H_2O}, X_{EtOH}, Y_{H_2O}, and Y_{EtOH} are the weight fractions of water and ethanol in the feed and permeate, respectively. The data error confirm in the range of ±10%.

Contact Angle Measurement

The contact angle of water was measured by a FACE contact angle meter (CA-D type, Kyowa Interface Science Co. Ltd.). Water droplets (sessile drops, volume ca. 1.8×10^{-3} cm[3]) were placed on the membrane covered with a fixing knob. After 10 s the dimensions of the droplets were measured. The droplets were small enough to be approximated as spheres. The contact angle was then calculated by the following equation:

$$\text{contact angle} = 2 \tan^{-1} (h/r),$$

where h and r are the height and the radius of the spherical segment, respectively.

Table I Contact Angle of Plasma-Treated Polysulfone Membranes

Plasma Treatment Conditions	Contact Angle H_2O
Untreated	76.6
AAm	
10 W, 20 s	39.2
10 W, 60 s	37.0
10 W, 120 s	25.2
10 W, 300 s	31.0

Grafting condition: acrylamide 10 wt % aqueous solution. Polymerization time: 2 h. Polymerization temperature: 60°C.
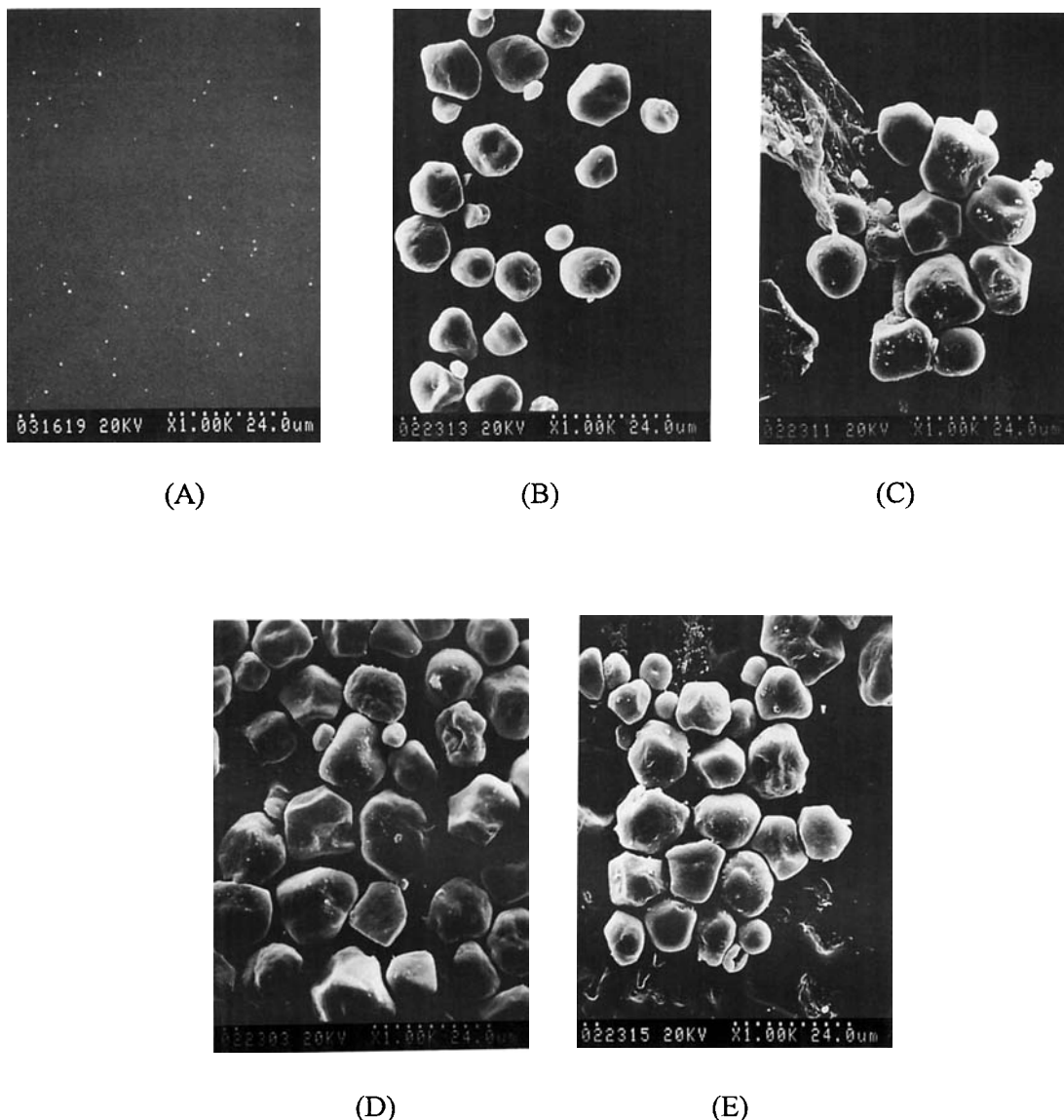
(A)   (B)   (C)

(D)   (E)

Figure 2   SEM micrographs of membrane surface: (A) unmodified PSF membrane; AAm-
p-PSF membrane; AAm-p-PSF membrane at 10 W and: (B) 20 s, (C) 60 s, (D) 120 s, and
(F) 300 s.

Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA data were obtained by using a Perkin–Elmer PHI 590 SAM/ESCA instrument, equipped with a Digital PDP 11/04 computer. The spectra were collected using the exciting radiation of MgK (h_ν = 1253.6 eV). The operation pressure was lower than 5×10^{-8} Pa and the power was 250 W. A survey scan (0–1000 eV binding energy) was run at an analyzer pass energy of 100 eV to determine the element composition of the PSF membrane. For high resolution studies, the pass energy was reduced to

25 eV. Atomic sensitivity factors (ASF) of the elements were taken into account to calculate the atomic ratios.

RESULTS AND DISCUSSION

Influence of Plasma Treatment Time on Grafting Yield

In this work, the AAm-p-PSF permselective membrane was prepared by two steps: the plasma activation of the surface of PSF substrate and the graft
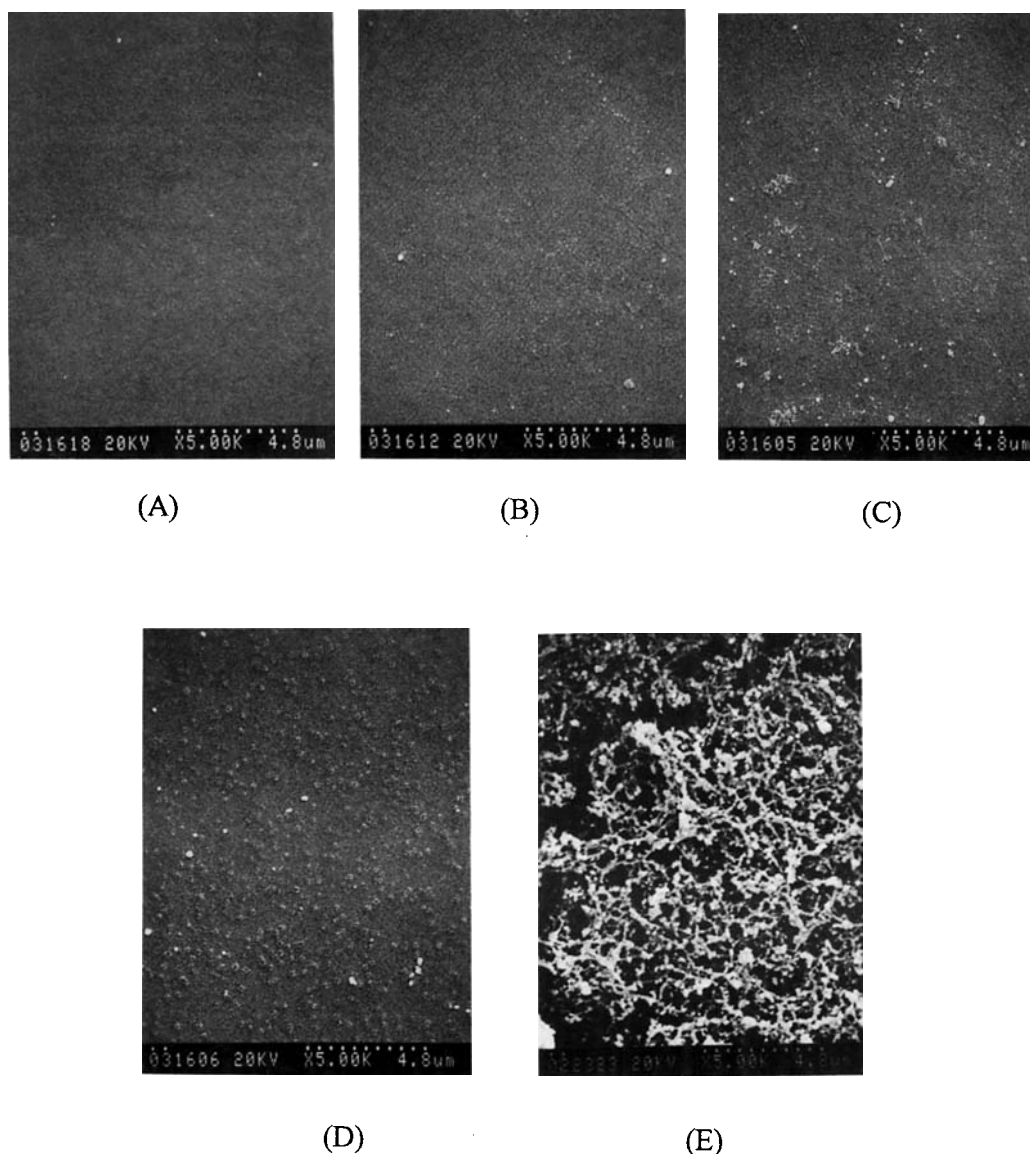
(A)

(B)

(C)

(D)

(E)

Figure 3   Effect of plasma treatment time on the PSF surface morphology. The plasma treatment power is 10 W and (A) 0 s, (B) 60 s, (C) 120 s, (D) 300 s, and (F) 600 s.

polymerization of the AAm monomer.[10] To find the optimal condition for plasma treatment, the dependence of the grafting yield of AAm on the plasma treatment time was investigated. Figure 1 shows the relationship between the plasma treatment time and the grafting yield. It can be seen that, when the plasma treatment time is less than 120 s, the grafting yields increase with increasing treatment time. This result was expected because the plasma can activate the substrate surface. However, when the treatment time is larger than 120 s, the grafting yields decrease as the treatment time increases. This trend can be explained by the fact that the plasma etching effect increases as the treatment time increases.[14] In our opinion, the occurrence of the maximum grafting yield stems from the competition between the surface activation and the surface etching.

The results discussed in the preceding paragraph were further confirmed by the SEM analysis and the water contact angle measurement. The SEM micrographs shown in Figure 2 indicate that the grafted poly(AAm) layer thickens the membrane surface and that the maximum grafting yield occurs at a treatment time of 120 s. The water contact angle experiment was used to estimate the surface hydrophilicity, an indication of the grafting amount of AAm. A larger contact angle indicates less hydrophilicity, suggesting that less AAm is grafted.[15] The

Table II Elemental Composition of Polysulfone Membranes with Plasma Deposition by ESCA

Plasma Treatment Condition	Relative Peak Intensity Ratio	
	N/C	S/C
Untreated	23	192
AAm		
10 W, 20 s	134	47.3
10 W, 60 s	138	1.31
10 W, 120 s	144	0

Grafting condition: acrylamide 10 wt % aqueous solution. Polymerization time: 2 h. Polymerization temperature: 60°C.

results are shown in Table I. It can be seen that the contact angle of the untreated PSF membrane is 76.6°, much higher than the plasma treated membrane. A minimum contact angle (25.2°) appears at the treatment time of 120 s. These results completely support the data shown in Figure 1.

In addition, the effect of plasma treatment time on the surface morphology of the PSF membrane is depicted in Figure 3. The results show that the etching effect increases with increasing plasma treatment time.[14] The membrane surface begins to form microcracks as the plasma treatment time is increased to 300 s, resulting in a rough surface. This observation agrees well with the results shown in Table I.
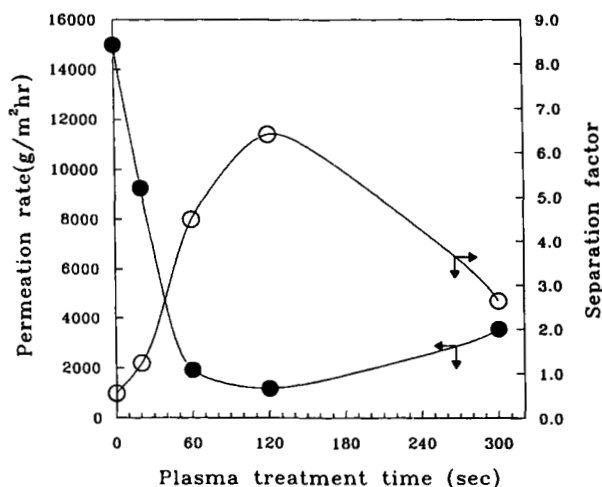

Figure 5 Effect of feed concentration on the total permeation rate and H_2O permeation rate of AAm-p-PSF membranes. Feed temperature 25°C, plasma treatment conditions 10 W and 120 s, grafting conditions 10 wt %, AAm aqueous solution, 2 h at 60°C. (○, □) Un-ionized grafted membranes and (●, ■) ionized grafted membranes.

Surface Analysis by ESCA

Because the graft polymerization behavior of the AAm-p-PSF membrane is drastically affected by the plasma treatment time, it is interesting to investigate the influence of plasma treatment conditions on the surface properties of PSF membranes. ESCA was used to analyze the composition of the mem-

Figure 4 Effect of plasma treatment time on (●) permeation rate and (○) separation factors. Operation conditions: 25°C, 90 wt % ethanol aqueous solution, plasma treatment power 10 W.
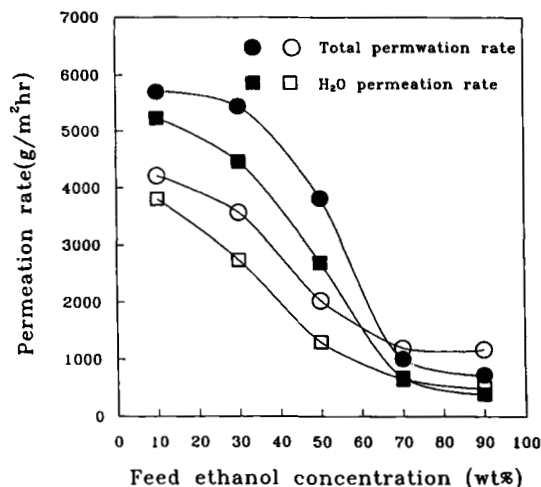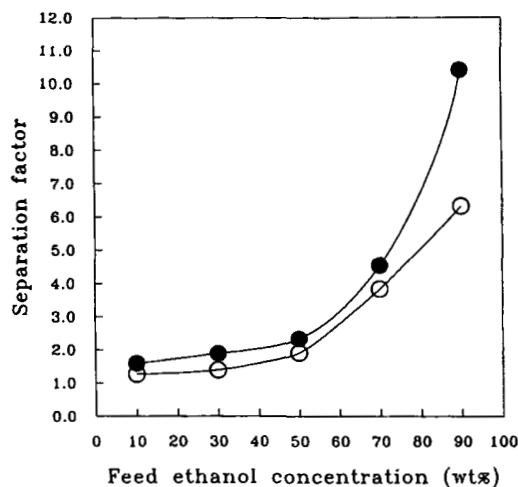

Figure 6 Effect of feed concentration on separation factors of AAm-p-PSF membrane. Feed temperature 25°C, plasma treatment conditions 10 W and 120 s, grafting conditions 10 wt % AAm aqueous solution, 2 h at 60°C. (○) Un-ionized grafted membranes and (●) ionized grafted membranes.
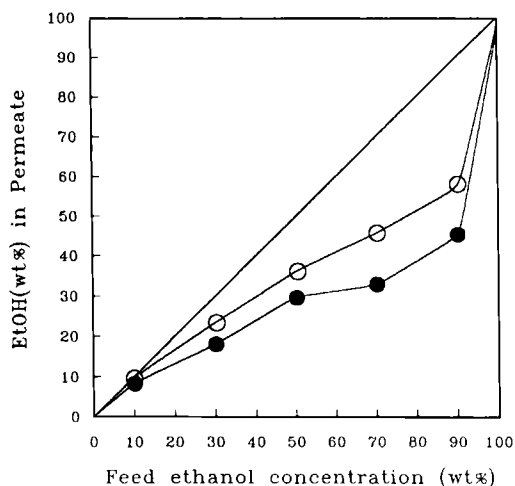
Figure 7 Effect of feed concentration on the ethanol permeation rate of AAm-p-PSF membrane. Feed temperature 25°C, plasma treatment conditions 10 W and 120 s, grafting conditions 10 wt % AAm aqueous solution, 2 h at 60°C. and (O) Un-ionized grafted membranes and (●) ionized grafted membranes.

brane surface and the results are shown in Table II. It can be seen that the relative peak intensity ratio of N_{1s} (400 eV)/C_{1s} (284 eV) (nitrogen/carbon) increases and the S_{2p} (165 eV)/C_{1s} (284 eV) (sulfur/carbon) decreases with increasing plasma treatment time. Meanwhile, the N_{1s} (400 eV)/C_{1s} (284 eV) ratio of the AAm-p-PSF membrane is higher than that of the untreated PSF membrane. When the amide group on the graft layer of the AAm-p-PSF membrane increases, the relative peak intensity at N_{1s} (400 eV) should increase, and the relative peak intensity ratio of S_{2p} (165 eV)/C_{1s} (284 eV) should decrease. Therefore, the results suggest that the graft layer gradually covers the PSF membrane as the plasma treatment time increases. It should be noted that the S_{2p} (165 eV)/C_{1s} (284 eV) ratio is equal to zero for the 10 W/120 s plasma treatment condition, indicating that the surface of the substrate PSF membrane is completely covered with the graft AAm layer.[12]

Effect of Plasma Treatment Time on Pervaporation Performance

Figure 4 shows the effect of plasma treatment time on the separation factor and the permeation rate of the AAm-p-PSF membrane when applied in pervaporation. The separation factor increased as the plasma treatment time increased to 120 s and then decreased as the plasma treatment time increased further. Meanwhile, the permeation rate varied in-

versely with the separation factor. These results can be explained by the fact that the grafting yield increases with increasing plasma treatment time, as does the hydrophilicity of the AAm-p-PSF membrane. Thus, the hydrogen-bonding interaction between the AAm-p-PSF membrane and the water molecules in the feed solution is enhanced, resulting in an increase in the separation factor. Nevertheless, an increase in the plasma treatment time may also enhance the AAm-p-PSF membrane thickness, which accounts for the decrease of permeation rate. In addition, for a plasma treatment time longer than 120 s, the etching effect reduces the membrane hydrophilicity, resulting in a decrease in the separation factor.

Effect of Feed Composition on Pervaporation Performance

The effect of the composition of feed mixtures on the pervaporation performances of the un-ionized and ionized AAm-p-PSF membranes for 10 W/120 s plasma treatment conditions are shown in Figures 5 and 6. Both the total permeation and water permeation rates decrease with an increase in the ethanol concentration of the feed solution while the separation factor increases. These results might be due to the plasticizing effect of water. When the water concentration in the feed solution is lower, the amorphous regions of the membrane are less swollen.[16] Therefore, the mobility of polymer chains decreases and the energy required for diffusive transport increases, resulting in the decrease of permeation rate.

In general, hydrophilic membranes have more polar groups and stronger hydrogen-bonding interactions with water. Therefore, the separation factor of the PSF membrane for pervaporation of aqueous alcohol solution can be enhanced by grafting the hydrophilic AAm on it. Furthermore, compared with the un-ionized AAm-p-PSF membrane, the ionized AAm-p-PSF membrane has a higher separation factor and permeation rate. These phenomena can be accounted for by the fact that the ionization of the amide group can enhance the hydrophilicity of the AAm-p-PSF membrane. Figure 7 shows the ethanol permeation curve of the ethanol-water mixture through the un-ionized and ionized AAm-p-PSF membrane. The permeate composition curve lies under the diagonal line, indicating that water is preferentially selected due to the highly hydrophilic graft layer.

CONCLUSION

In this study, a highly hydrophilic AAm layer was successfully grafted on the surface of PSF membranes by plasma treatment. This hydrophilic thin layer can greatly improve the pervaporation performance of PSF membranes. The pervaporation performance of the grafted membrane can be further improved by ionization. A separation factor of 10.4 and a permeation rate of 718.1 g/m^2 h were obtained. In addition, the composition of the membrane surface was analyzed to prove that AAm had been successfully grafted.

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