

Pervaporation of Water–Ethanol Mixtures through Plasma Graft Polymerization of Polar Monomer onto Crosslinked Polyurethane Membrane

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ABSTRACT: To improve the pervaporation performance, the plasma post-graft polymerization of 2,3-epoxypropylmethacrylate (EPMA) onto the crosslinking polyurethane (CPU) membrane, EPMA-*g*-CPU, was synthesized in this study. The crosslinking between soft–soft hydroxyl-terminated polybutadiene (HTPB) segments were prepared by the introduction of benzoyl peroxide to the HTPB-based PU membrane. The effect of plasma treatment time and plasma supply power on the grafting yield was discussed. The optimum plasma treatment conditions were 10 W supply power and 120 s treatment time. The surface properties of the EPMA-*g*-CPU membrane were characterized by Fourier transform infrared spectroscopy, electron spectroscopy for chemical analysis, and a contact angle meter. A separation factor of 97 and a 240 g m⁻² h⁻¹ permeation rate through the EPMA-*g*-CPU membrane with a 4.81 mg/cm² grafting yield for a 90 wt % feed ethanol concentration were obtained. Compared with ungrafted CPU membrane, the EPMA-*g*-CPU membrane effectively improved the pervaporation performances. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1789–1797, 1998

Key words: crosslinking; polyurethane; plasma; post-graft; pervaporation

INTRODUCTION

From the energy saving point of view, pervaporation can be alternative to the azeotropic distillation. A large amount of polymeric materials have been used in order to prepare pervaporation membranes for dehydration purposes, such as cellulose, poly(vinyl alcohol), poly(dimethylsiloxane), chitosan, silicone rubber, nylon-4, poly(tetrafluoroethylene), ion-exchange membrane, and polyelectrolyte complex, and have been given much attention.^{1–13} Polyurethane possesses good membrane

formation and chemical resistance. It can be considered as a membrane material. However, due to the low glass transition temperature of the hydroxyl-terminated polybutadiene (HTPB) soft segment, the HTPB-based polyurethane (PU) exhibit the low tensile strength and breaking strength at room temperature. The crosslinking of PU polymers were usually obtained by the introduction of diol and triol mixtures to the PU prepolymer.^{14,15} In this study, the crosslinking between soft–soft HTPB segments were prepared by the introduction of benzoyl peroxide to the HTPB-based PU membrane. Additionally, in the hope of further increasing permselectivity properties, a hydrophilic vinyl monomer, that is, 2,3-epoxypropylmethacrylate (EPMA), was used to

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graft onto crosslinked PU membrane by plasma graft polymerization. It is well known that the plasma surface treatment can be utilized to change the surface energy of polymeric films.¹⁶ The plasma deposition method has been popularly used to increase biomedical compatibility.¹⁷ A coating of plasma-polymerized ultrathin film permanently changes the surface energy of a substrate without altering bulk properties of the materials.^{18,19} The purpose of this study was prepared a water-permeable PU membrane by the following two steps: the plasma activation of the substrate membrane, and then the hydrophilic monomer grafted onto the surface of the substrate membrane. The effect of plasma treatment conditions on the surface properties of EPMA-g-CPU membrane were discussed. In addition, the effects of feed solution concentration and degree of swelling on the pervaporation performances were investigated.

EXPERIMENTAL

Materials

The uncrosslinking PU was polymerized as described previously.²⁰ The polymer solution was precipitated and extracted in acetone and methanol, respectively, then dried in a vacuum oven for 24 h. Benzoyl peroxide (BPO) was used as crosslinking agent. The EPMA monomer was purchased from Merck Co. and purified by reduced pressure distillation.

Membrane Preparation

The crosslinked PU membrane was made by phase inversion process. The casting solution in a cone bottle, consisting of 12 wt % PU polymer in tetrahydrofuran (THF), was stirred above 24 h, then BPO was added for crosslinking. The detailed procedure is described in a previous article.²¹

Plasma Graft Polymerization

A tubular deposition system externally equipped with capacity coupling electrodes (Model RFG-300, Samco Ltd., Japan) was used in this study.²² The substrate membrane was placed in the center between two electrodes that were 9 cm apart. The tube reactor i.d. is 5 cm. The tube was evacuated to 0.02 torr. The plasma was ignited at a frequency of 13.56 MHz with power of 5–50 W for 60–360 s. After the membrane was treated by

plasma, the degassed EPMA–ethanol 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 1.5–3 h. Ethanol was used to wash off the homopolymer for 24 h and then dried at room temperature. Fourier transform infrared (FTIR) spectroscopy was used obtained at 1 cm⁻¹ resolution using a Shimadzu model FTIR-8201 PC.

Pervaporation Experiments

A traditional pervaporation apparatus was used in this study.²³ The effective membrane area was 10.17 cm². A vacuum pump maintained the downstream pressure at 3–5 mmHg. 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 absorbed in the membrane were measured by gas chromatography (GC; China Chromatography 8700T). The separation factor, $\alpha_{\text{H}_2\text{O}/\text{EtOH}}$, was calculated from

$$\alpha_{\text{H}_2\text{O}/\text{EtOH}} = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{EtOH}}}{X_{\text{H}_2\text{O}}/X_{\text{EtOH}}}$$

where $Y_{\text{H}_2\text{O}}$, Y_{EtOH} and $X_{\text{H}_2\text{O}}$, X_{EtOH} are the weight fraction of water and ethanol in the permeate and feed, respectively.

Preferential Sorption Measurements

The sorption apparatus used in this study was the same as reported in the previous study.²⁴ A membrane was immersed in ethanol–water mixtures for 24 h. It was subsequently blotted between tissue paper to remove adherent solvent and placed in the left half of a twin tube setup. The system was evacuated while the left tube was heated with hot water and the right one was cooled in liquid N₂. The composition of the condensed liquid in the right tube was determined by GC.

Contact Angle Measurements

The contact angle of water was measured with a face contact angle meter CA-D type (Kyowa Interface Science Co. Ltd.). Sets of droplets (sessile drops; volume of approximately 1.8 × 10⁻³ cm³) of water were placed on a membrane covered fixing knob. The dimensions of the droplets were mea-

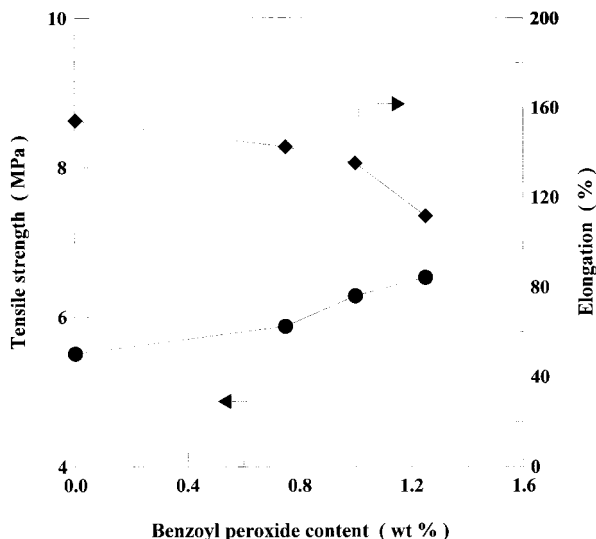


Figure 1 Effect of crosslinking agent concentration on the mechanical properties of CPU membrane: (●) tensile strength; (◆) elongation. Operating conditions are as follows: crosslinking time, 6 h; crosslinking temperature, 60°C.

sured approximately 10 s after placing the droplets on the knob. The droplets must be small enough so that their shape approximates a sphere. The contact angle was calculated by the following condition:

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

where h is the height of the spherical segment, and r is the radial of the spherical segment.

Mechanical Properties Measurement

The tensile strength and elongation measurement of crosslinked PU membrane was carried out by using the Instron Co. Model 4302 instrument with a testing method of ASTM D-638 and D-882.

RESULTS AND DISCUSSION

Effect of the Degree of Crosslinking on the Mechanical Properties of the CPU Membrane

A HTBD-based PU was synthesized by direct polycondensation. The polymer compositions of diol, diisocyanate, and chain extender were HTPB, 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI), and 1,4-butadiene, respectively. Due to the very low glass transition temperature and low temperature flexibility of the HTPB soft segment, the HTPB-based PU exhibit the low tensile strength and

breaking strength at room temperature.²¹ Hence, the stability of PU is drastically affected by the plasma treatment procedure and the swelling of the feed solution. These disadvantages can be overcome by crosslinking method. Thus, it is interesting to investigate the influence of the degree of crosslinking on the mechanical properties of the CPU membrane. Figure 1 shows that the tensile strength increased and the elongation decreased with increasing the crosslinking agent concentration in polymer solution from 0–1.25 wt % (g -BPO/ g -PU). These phenomena might be due to the fact that the polymer chain mobility and flexibility decreased as the crosslinkage between HTPB soft segments was formed, resulting in the increased tensile strength and the decreased elongation. Additionally, all of the CPU membrane have higher tensile strength than that of the uncrosslinked PU membrane. Based on the request of the stability and reproducibility of membrane, the CPU membrane with a composition of 1 wt % (g -BPO/ g -PU) was used as the plasma pretreatment substrate.

Effect of Plasma Treatment Condition on the Grafting Yield of EPMA- g -CPU Membrane

A EPMA- g -CPU membrane was prepared by the following two steps: the plasma activation of the

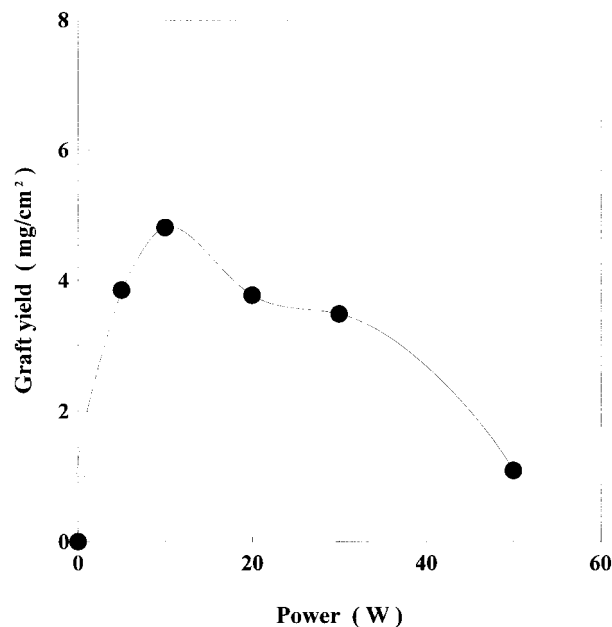


Figure 2 Effect of plasma power on the grafting yield of EPMA- g -CPU membrane: plasma treatment time, 120 s; grafting condition, 10 wt % EPMA solution (solvent : ethanol); polymerization time, 2 h; polymerization temperature, 60°C.

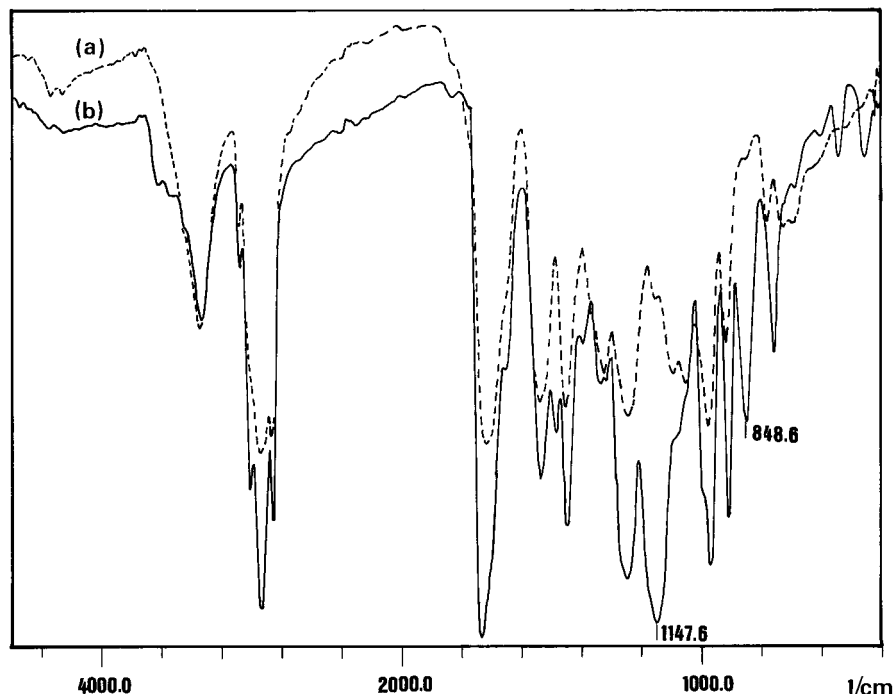


Figure 3 FTIR spectra of (a) unmodified CPU membrane and (b) EPMA-*g*-CPU membrane: plasma treatment condition, 10 W/120 s; grafting condition, 10 wt % EPMA solution (solvent : ethanol); polymerization time, 2 h; polymerization temperature, 60°C.

substrate membrane (CPU), and then the hydrophilic monomer grafted onto the surface of the substrate membrane. In order to study the effect

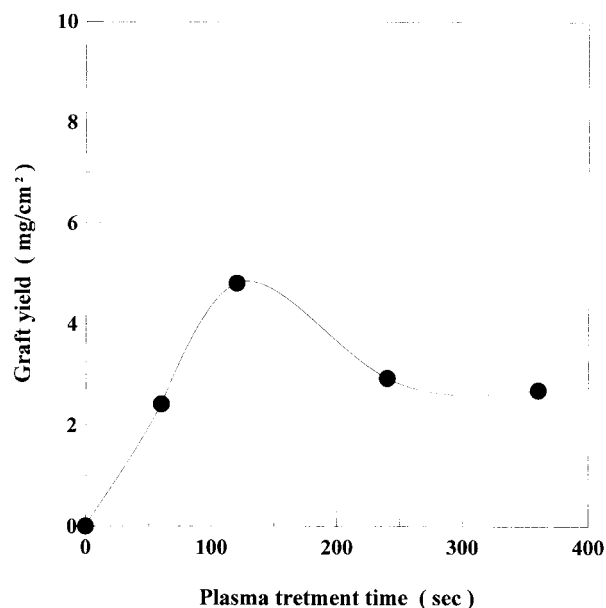


Figure 4 Effect of plasma treatment time on the grafting yield of EPMA-*g*-CPU membrane: plasma power, 10 W; grafting condition, 10 wt % EPMA solution (solvent : ethanol); polymerization time, 2 h; polymerization temperature, 60°C.

of plasma treatment condition on the modified CPU membranes, the plasma supply power was varied from 5 to 50 W at a fixed deposition time 120 s. Figure 2 shows the relationship between the plasma supply power and the grafting yield. It can be seen that the grafting yield increases with the plasma supply power up to 10 W; whereas, beyond this supply power, the grafting yield decreases. These results can be illustrated such that an increase in supply power may enhance the active site on the substrate membrane surface, resulting in the probability of creating grafted polymer chains with monomer increased. Nevertheless, for a supply power higher than 10 W, microcracks and surface etching induced by plasma, leads to a decrease in grafting yield. Additionally, Figure 3 shows the FTIR spectra of the crosslinked polyurethane membrane (a) and the EPMA-*g*-CPU membrane (b). Comparison between spectra (a) and (b) shows that two new characteristic peaks at 848.6 cm^{-1} ($\begin{matrix} \text{C} & - & \text{O} \\ \backslash & & / \\ & \text{O} & \end{matrix}$)

and 1147.6 cm^{-1} (—O—) were observed. These peaks were not observed at all in CPU membrane. These indicated that the EPMA-*g*-CPU membrane was successfully synthesized. Figure 4 shows the effect of plasma treatment time on the grafting yield of EPMA-*g*-CPU membrane at 10

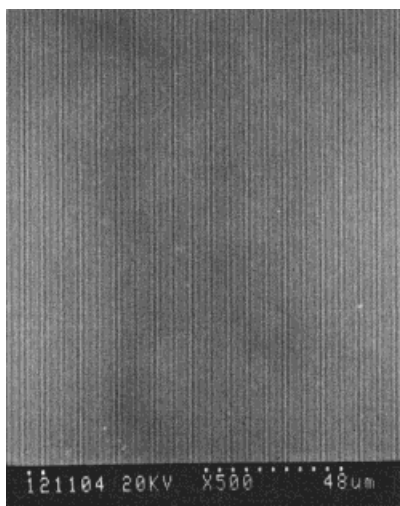
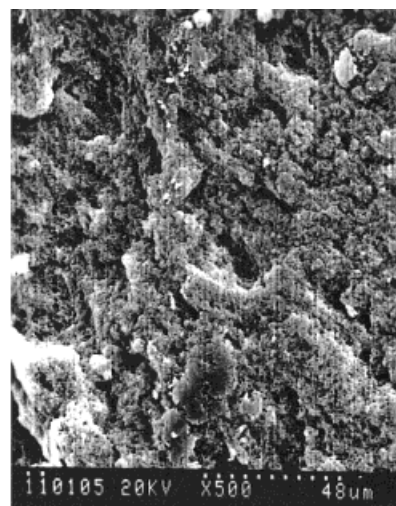
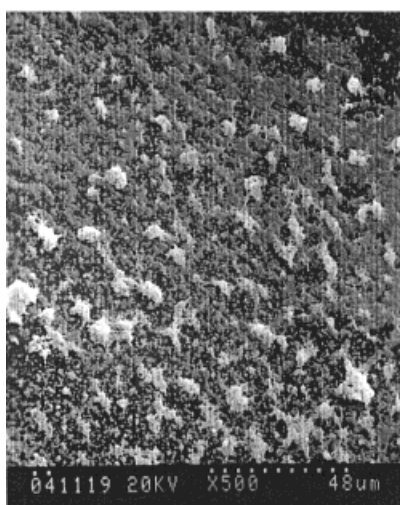
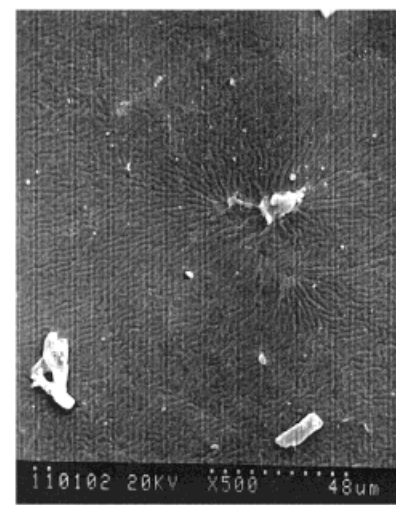

(a)

(b)

(c)

(d)

Figure 5 Surface views of an SEM photograph: (a) unmodified CPU membrane; (b) EPMA-*g*-CPU membrane (10 W 120 s); (c) EPMA-*g*-CPU membrane (30 W 120 s); (d) EPMA-*g*-CPU membrane (50 W 120 s). Conditions are as follows: grafting condition, 10 wt % EPMA solution (solvent : ethanol); polymerization time, 2 h; polymerization temperature, 60°C.

W plasma supply power. A similar trend was observed, as indicated in Figure 2. This is verified by scanning electron microscopy (SEM), as shown in Figure 5. In Figure 5, it is shown that the

grafted EPMA layer thickens the membrane surface and that the thickness increases with increasing the supply power up to 10 W. The membrane surface begins to form microcracks and/or

Table I Elemental Composition of CPU Membranes with Plasma Treated by ESCA

Plasma Treatment Conditions	Graft Yield (mg/cm ²)	Relative Peak Intensity Ratio O/C
Untreated	0	0.0412
5 W, 120 s	3.85	0.2979
10 W, 120 s	4.81	0.3373
30 W, 120 s	3.48	0.2993
50 W, 120 s	1.09	0.2591

Plasma treatment time, 120 s; grafting condition, 10 wt % EPMA solution (solvent: ethanol); polymerization time, 2 h; polymerization temperature, 60°C.

surface etching as the supply power is further increased. These observations correspond very well with the results indicated in Figures 2 and 4. Furthermore, it is interesting to investigate the influence of plasma treatment conditions on the surface properties of EPMA-*g*-CPU membrane. ESCA was used to analyze the composition of the membrane surface, and the results are shown in Table I. It shows that the relative peak intensity ratio $O_{1s}(535\text{eV})/C_{1s}(284\text{eV})$ increased with increasing the plasma supply power up to 10 W, then decreased. These phenomena must be due to the fact that for the hydrophilic monomer (EPMA) structure content epoxy ring and ester group, when EPMA was grafted onto CPU membrane, the relative peak intensity of $O_{1s}(535\text{eV})/C_{1s}(284\text{eV})$ increased. Therefore, the results suggest that the graft layer gradually grows under the 10 W supply power. This result completely supports the data as shown in Figure 2. In addition, the water contact angle experiment was used to estimate the surface hydrophilicity. A higher contact angle value indicates less hydrophilicity, suggesting that lower grafting yield was obtained. The result is shown in Table II. It can be seen

Table II Contact Angle of Plasma-treated CPU Membranes

Plasma Treatment Conditions	Graft Yield (mg/cm ²)	Contact Angle of Water
Untreated	0	88.5
10 W, 120 s	4.81	35.5
30 W, 120 s	3.48	67
50 W, 120 s	1.09	76.75

Plasma treatment time, 120 s; grafting condition, 10 wt % EPMA solution (solvent: ethanol); polymerization time, 2 h; polymerization temperature, 60°C.

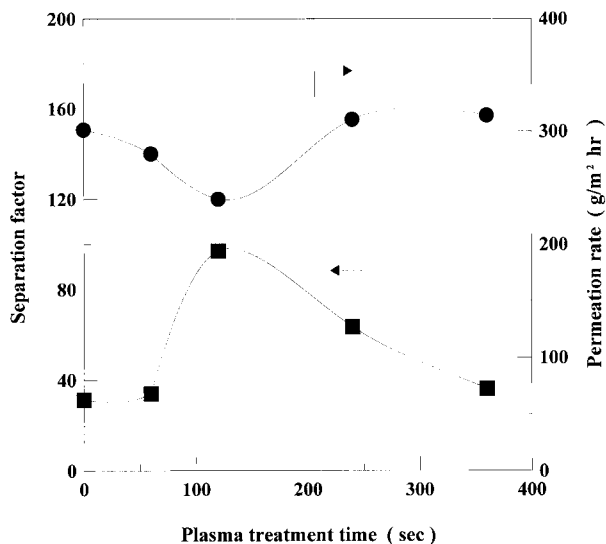


Figure 6 Effect of plasma treatment time on the pervaporation performances for EPMA-*g*-CPU membrane: (●) permeation rate; (■) separation factor. Conditions are as follows: plasma power, 10 W; grafting condition, 10 wt % EPMA solution (solvent : ethanol); polymerization time, 2 h; polymerization temperature, 60°C; operation condition, 25°C, 90 wt % ethanol aqueous solution.

that the water contact angle of the ungrafted CPU membrane is much higher than that of the EPMA-*g*-CPU membrane. A minimum contact angle appears at 10 W/120 s plasma treatment conditions.

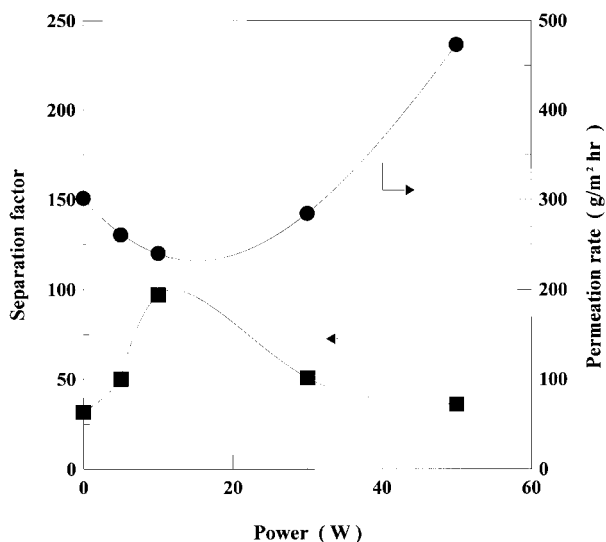


Figure 7 Effect of plasma power on the pervaporation performances for EPMA-*g*-CPU membrane: (●) permeation rate; (■) separation factor. Conditions are as follows: plasma treatment time, 120 s; grafting condition, 10 wt % EPMA solution (solvent : ethanol); polymerization time, 2 h; polymerization temperature, 60°C; operation condition, 25°C, 90 wt % ethanol aqueous solution.

Table III Effect of Polymerization Time on the Graft Yield Permeation Rate and Separation Factor

Polymerization Time (h)	Graft Yield (mg/cm ²)	Permeation Rate (g m ⁻² h ⁻¹)	Separation Factor	PSI × 10 ⁻⁴
1.5	1.48	352	49	1.7
2	4.81	240	97	2.3
2.5	7.07	384	53	2.0
3	8.2	defect	—	—

Plasma treatment condition, 10 W/120 s; grafting condition, 10 wt % EPMA solution (solvent: ethanol); polymerization temperature, 60°C; operation condition, 25°C, 90 wt % ethanol aqueous solution.

These results agree with the results shown in Figures 2 and 4. Consequently, the optimum treatment condition in this article is 10 W supply power and 120 s treatment time.

Effect of Plasma Conditions on the Pervaporation Performance of EPMA-*g*-CPU Membrane

The effect of plasma treatment time and supply power on the pervaporation performances of a 90 wt % aqueous alcohol solution through the EPMA-*g*-CPU membrane are shown in Figures 6 and 7. Similar results of permeation rate and separation factor were obtained for the above studies. That is, the separation factor increased with the plasma treatment time and plasma supply power up to 120 s and 10 W, respectively, then decreased. In addition, the permeation rate has a minimum value at the 120 s of plasma treatment time and 10 W of plasma supply power. These phenomena might be due to the fact that the interaction of hydrogen bonding between the water molecules and the membrane increases with increasing the grafted layer (EPMA) at the plasma treatment time and supply power lower than 120 s and 10 W, respectively, resulting in increased water permselectivity. On the other hand, these results can be explained from the viewpoint of the hydrophilicity of the EPMA-*g*-CPU membrane. Because the hydrophilicity of EPMA-*g*-CPU is higher than that of the ungrafted CPU membrane. Thus, the water molecules preferentially dissolve in the EPMA-*g*-CPU membrane and also predominantly diffuse through the membrane, resulting in an increase in the separation factor. Moreover, the plasma etching effect becomes more important as the supply power and treatment time further increase. Hence, the separation factor decreases.

Pervaporation Properties of EPMA-*g*-CPU Membrane for Alcohol–Water Mixtures

The CPU membrane was pretreated with 10 W/120 s plasma conditions and then grafted poly-

merized with the EPMA monomer. The grafted yield and pervaporation performances are shown in Table III. It shows that the optimum pervaporation results were obtained by EPMA-*g*-CPU membrane with 10 W/120 s plasma pretreatment conditions and 2 h grafted polymerization time, giving a grafted yield of 4.81 mg/cm², a separation factor of 97, a permeation rate of 240 g m⁻² h⁻¹, and a 2.3 × 10⁴ pervaporation separation index (PSI) value. The effect of feed ethanol concentration on the pervaporation performances for the ungrafted CPU membrane and EPMA-*g*-CPU membrane with a 4.81 mg/cm² grafted yield are shown in Figure 8. The separation factor decreases, and the permeation rate increases as the feed ethanol concentration increases. These phenomena might be due to the plasticizing effect of ethanol. Generally, the hydrophobic membrane has a strong interaction with alcohol. When the ethanol concentration in the feed solution is higher, the amorphous region of the membrane is more swollen. Therefore, the polymer chains mobility increases, and the energy barrier for molecules diffusion decreases, resulting in the permeation rate increases. Furthermore, when the degree of swelling of the membrane in the mixture was large, water permeated through the membrane in spite of its low affinity toward the membrane. Thus, the separation factor increased with the increasing of the feed ethanol concentration. Additionally, the pervaporation performance of EPMA-*g*-CPU membrane is better than that of the ungrafted CPU membrane in the range of 10–90 wt % feed ethanol concentration. This may be due to hydrophilicity, and the hydrogen-bonding ability of the former is higher than that of the latter. Thus, a good pervaporation performances for EPMA-*g*-CPU membrane were obtained. The swelling degree decreases as the feed ethanol concentration decreases for the ungrafted CPU membrane and the EPMA-*g*-CPU membrane, as shown in Figure 9. These results correspond well with the results from the permeation rate and

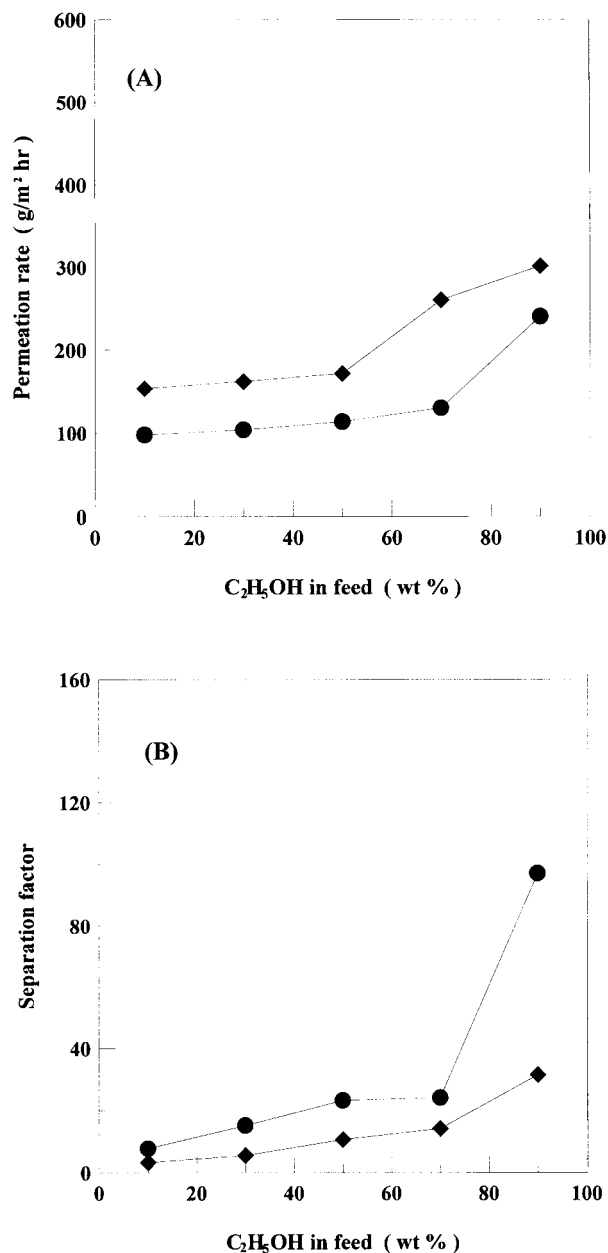


Figure 8 Effect of feed concentration on the pervaporation performances: (A) permeation rate and (B) separation factor. (♦) designates the CPU membrane; (●) designates the EPMA-g-CPU membrane (grafting yield 4.81 mg/cm²). The operation condition is 25°C.

separation factor studies of the ungrafted CPU membrane and the EPMA-g-CPU membrane, as indicated in Figure 8. The effects of solubility and diffusivity on membrane permselectivity and sorption experiments for the EPMA-g-CPU membrane with a 4.81 mg/cm² grafting yield for pervaporation of aqueous ethanol solution were made. The ethanol concentration in the membrane is higher than that in the permeate for the ethanol

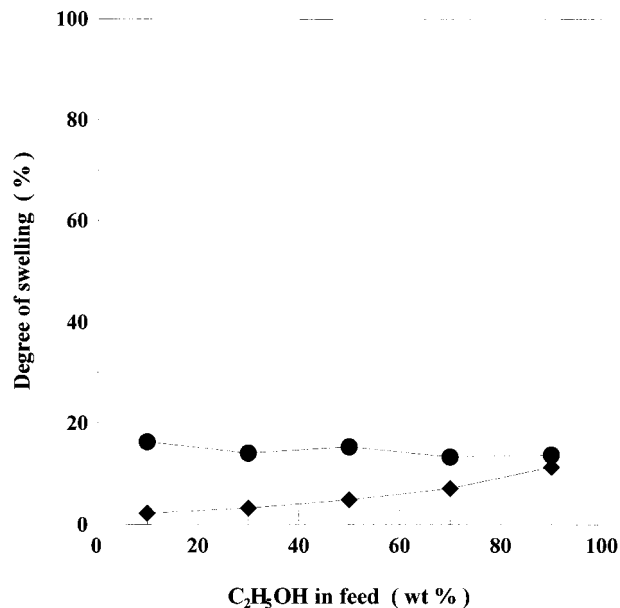


Figure 9 Effect of feed concentration on the degree of swelling: (♦) CPU membrane; (●) EPMA-g-CPU membrane (grafting yield 4.81 mg/cm²). The operation condition is 25°C.

feed concentration in the range of 10–90 wt %, as shown in Figure 10. These results can be explained by the very strong affinity between the ethanol molecules and the CPU substrate membrane. Additionally, once the water molecules are incorporated into the EPMA-g-CPU membrane, they can easily diffuse through the grafted mem-

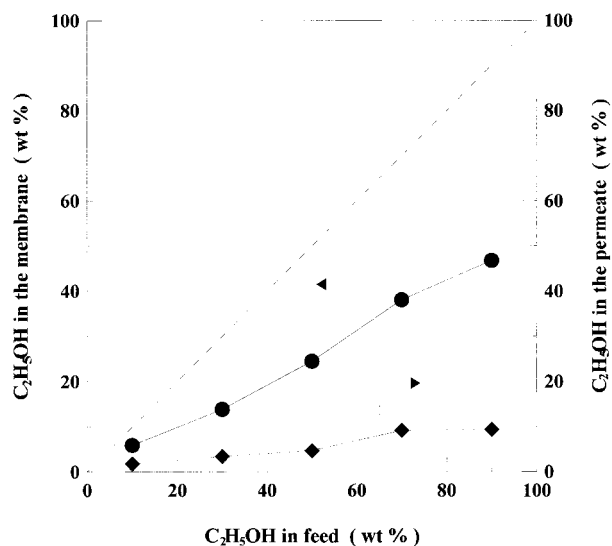


Figure 10 Effect of feed concentration on the ethanol concentration in the membrane and in the permeate of EPMA-g-CPU membrane: grafting yield, 4.81 mg/cm²; operation condition, 25°C.

brane because the interaction between the water molecules and grafted membrane is very weak and, also, the molecular size of water is smaller than that of ethanol. Therefore, the permeate and sorption composition curves lie under the diagonal line. The results of the degree of swelling of the EPMA-*g*-CPU membrane indicated in Figure 9 completely support the data shown in Figure 10.

CONCLUSION

From the pervaporation experiments of dehydration of aqueous ethanol solution, it can be concluded that the EPMA-*g*-CPU membrane effectively improved the pervaporation performances. The plasma treatment time and plasma supply power are important factors in controlling the grafting yield of the EPMA-*g*-CPU membrane. All of the membranes exhibited water selectivity during all process runs. The optimum pervaporation results were obtained by EPMA-*g*-CPU membrane with 10 W/120 s plasma pretreatment conditions and 2 h grafted polymerization time, giving a separation factor of 97, a permeation rate of $240 \text{ g m}^{-2} \text{ h}^{-1}$, and a 2.3×10^4 PSI value.

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