

Water-Ethanol Separation by Pervaporation Through Plasma Graft Polymerized Membranes

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Synopsis

Water-ethanol permselective membranes were prepared through plasma graft polymerization of acrylic acid, methacrylic acid, and acrylamide onto porous polypropylene film. In these membranes, the functions of permseparation and mechanical properties are shared respectively to the graft polymer layer and the substrate film. Higher permselectivity of water is achieved with the ionization of the acrylic acid and the methacrylic acid-grafted membranes. Permselectivity is dependent on the degree of grafting, and it is necessary to fill the pores of substrate film with graft polymers. Permseparation of water was investigated with respect to the feed ethanol concentration and also to the temperature dependence.

INTRODUCTION

Pervaporation which is carried out through a membrane across the heterogeneous phase between liquid and gas is a useful procedure for the separation of azeotropic and isomeric mixtures. In addition, much attention has been directed recently to the separation of water and alcohol from biomass products by this method. However, in order to apply this to the water-ethanol separation, more effective membranes must be developed and much greater efforts have been made recently.

There are two types of water-ethanol permselective membranes, water permselective and ethanol permselective. The former is much popular at present. For the water permselectivity, the membrane should be hydrophilic to attract water from the feed solution. Indeed, the conventional hydrophilic membranes such as cellulose and poly(vinyl alcohol) show higher permselectivity of water. Membranes which contain ionic groups have gained favor owing to their greater hydrophilicity. Water-ethanol separation by pervaporation through ionic membranes such as ion exchange membranes^{1,2} or copolymeric membranes containing ionic moieties³ have been investigated, and the better results on the water permselectivity have been reported.

Thus, the construction of membranes with more hydrophilicity seems to be more preferable for water permseparation. However, too much hydrophilicity often leads to the dissolution of the membrane in contact to the aqueous feed solutions. To avoid such defects, membranes are usually modified, for example by crosslinking.

A useful procedure to obtain the insoluble membranes lies in graft polymerization of hydrophilic monomers onto stable substrate film. Very hydrophilic layers, which should be soluble in the homopolymer state in the feed solution

can be immobilized to the substrate film to be effective for the water-permsepation. In this kind of composite membrane the mechanical and chemical stability is owed to the substrate film, and the permselective function to the grafted layer. We thus attempted to prepare the composite membrane with the hydrophilic layer on the porous substrate film by means of plasma graft polymerization, and the permsepation of water from water-ethanol mixture solution was investigated with pervaporation. Here the plasma process has been employed to initiate the graft polymerization, because the reaction is usually surface specific.

It is well known that polymer radicals are formed on the surface of polymeric materials by plasma surface treatments, and some of them can initiate graft polymerization of vinyl monomers. These reactions have been recognized for a long time and applied for the surface modification of polymers such as polyesters.⁴ However, plasma graft polymerization has not been considered as often as plasma surface treatments and plasma polymerization. This is because the total reaction process involved in the plasma graft polymerization is much more complicated, and sometimes the merit of gas phase reaction in plasma process is injured. Usually, much homopolymeric subproducts are formed during the graft polymerization, and it is necessary to remove them by washing. However, the advantages of plasma graft polymerization have been recognized once again. One such advantage is the durability of the properties of the modified surface. The surface characteristics enhanced by the graft polymerization do not change easily, while the properties caused by plasma surface treatments often suffer from the recession with aging.

Plasma graft polymerization has been applied to impart hydrophilicity on the pores of the porous membranes, and improvements of water permeation under pressure have been reported by Osada et al.⁵ In these membranes, the macropores remained and water was permeable through the pores. Water permeation rate was controlled according to the mechanochemically changed pore sizes in the graft-polymerized membranes. However, such macropores are undesirable for the liquid permsepation, for example in the case of the water-ethanol separation, because the solution is not changed and there is no separation through the pores. In order to construct the water-ethanol permselective membrane, the pores must be filled with the hydrophilic graft layer, through which a component in the feed solution can be selectively permeated via the diffusion-solution process.

In this study, we attempted to obtain the water-ethanol permselective membranes by plasma graft polymerization mainly using acrylic acid as a monomer. The graft-polymerized membranes can be fully ionized, and the much improved water-selective permsepation could be performed by pervaporation.

EXPERIMENTAL

Materials

Porous polypropylene film with the average pore size of 2000 Å (Celgard 2400) was used as a substrate. Acrylic acid, acrylamide, and methacrylic acid were graft polymerized. Acrylic acid and methacrylic acid were purified by

distillation under vacuum, and acrylamide by recrystallization from benzene-ethanol before graft polymerization.

Preparation of Membranes by Plasma Graft Polymerization

The composite membranes for permseparation were prepared as follows: porous polypropylene film was at first surface-treated by plasma and then the monomer was reacted onto the surface in the 5% aqueous solution. Grafting was conducted in solution state here, because the thicker layer of graft polymers was necessary for permseparation. Graft polymerization was also possible in the gaseous state of a monomer, but the growing rate was considerably low and much longer reaction time was necessary.

The substrate film ($6 \times 6 \text{ cm}^2$) was set in the reactor (3.0 cm in inner diameter and 24 cm in length), and the system was evacuated at $1.0\text{--}2.0 \times 10^{-3}$ torr* of flow pressure. Then, the substrate film was treated with glow discharge plasma at the frequency of 13.56 MHz. To prevent the defects of the substrate film caused by plasma, the lower plasma discharge at 10 W and the shorter plasma exposure time were employed. After the plasma surface treatments, the activated substrate film was reacted in the 30 mL of 5% aqueous monomer solution which had been previously degassed under vacuum. Graft polymerization was carried out at 40, 50, and 60°C for 1.0 to 4.0 h, and the composite membranes with varying amounts of grafting were obtained.

Graft polymerization was performed without contact to air after plasma surface treatments, because the polymerization was seriously suppressed by reaction with oxygen. After polymerization ended, the membrane was washed and soaked in distilled water overnight to remove the homopolymers.

Ionization of acrylic acid and methacrylic acid graft polymerized membranes was done by treating with 2% aqueous sodium hydroxide solution at room temperature for about one hour. The ionization to carboxylate was confirmed from the infrared peak transfer, for example from 1710 cm^{-1} to 1570 cm^{-1} in the acrylic acid grafted membranes.

Pervaporation Experiments

Procedure of pervaporation was principally the same as described in the literature.⁶ The membrane chosen for use was 4.7 cm in diameter and placed in the stainless steel pressure holder. As a feed, aqueous ethanol solutions with concentrations of 0, 20, 50, 70, and 90% were examined. (Exact concentration of ethanol in the feed solution was confirmed by gas chromatography in each experiment as well as that in permeate.) About 30 mL of the feed solution was supplied and the other face of the membrane was evacuated at less than 2×10^{-2} torr under conditions where high blank values obtained. During the pervaporation, the system pressure ranged from 1×10^{-1} to 1.0 torr depending on the permeation rate. The pervaporation experiments were usually carried out at 40°C, and were also made in the temperature range from 30°C to 60°C to observe temperature dependence and to obtain the activation energy of permeation.

*1.0 torr is corresponding to 1.3332×10^2 Pa in SI unit.

The permeate was collected in a cold trap in liquid nitrogen. The flux was calculated from the weight, and given in kg/m² h. Water and ethanol were analyzed with gas chromatography, and the relative concentration was obtained from the peak strength.

Separation factor of water ($\alpha_{\text{ethanol}}^{\text{water}}$) was calculated from the concentrations of these components in feed and permeate as in the following equation:

$$\alpha_{\text{ethanol}}^{\text{water}} = (X_{\text{water}}/X_{\text{ethanol}})/(Y_{\text{water}}/Y_{\text{ethanol}})$$

where X_{water} and X_{ethanol} are the concentrations of water and ethanol in the permeate, and Y_{water} and Y_{ethanol} are those in the feed solution.

RESULTS AND DISCUSSION

Plasma Graft Polymerization

Plasma graft polymerization was performed through two successive processes: plasma surface activation by inert gases, followed by the graft polymerization of monomers. Therefore, the yield of grafting was naturally dependent on the factors derived from these processes.

The dependence of the grafting yield on the plasma treatments was investigated at first. Figure 1 shows the dependence of the grafting yield of acrylic acid on the plasma treatment periods. Discharge power was 10 W and the residue gas was used for plasma at the flow pressure of 2.0×10^{-3} torr. Grafting was carried out at 50°C for 1, 2, and 4 h, respectively. The grafting yield was measured by the amount of polymer grafted on the surface of porous polypropylene film in the unit of mg/cm². The yields increased with the plasma treatment time.

Formation of polymer radicals by plasma pretreatments is indispensable for the initiation of graft polymerization, and in addition, it must be pointed out that the hydrophilic change of the surface also plays an important role on the graft polymerization carried out in the aqueous solution here. In other words, the improvements of affinity of the monomer to the substrate surface is effective to induce the graft polymerization. This can be noticed through the

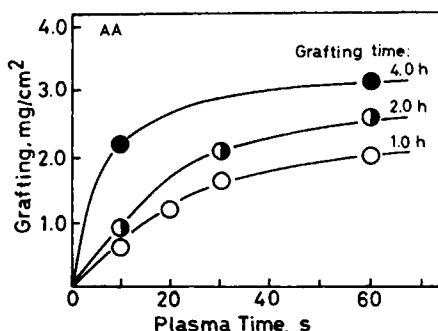


Fig. 1. Dependence of graft polymerization of acrylic acid onto porous polypropylene film on plasma treatment time (grafting condition; 5% aqueous monomer solution, 50°C).

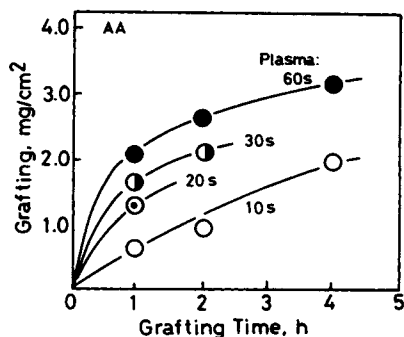


Fig. 2. Dependence of graft polymerization of acrylic acid onto porous polypropylene film on grafting time (grafting condition; 5% aqueous monomer solution, 50°C).

observation that the graft polymerization does not take place at all on the untreated substrate film.

The effect of grafting condition was next investigated. Figure 2 shows the dependence of graft polymerization of acrylic acid on the grafting time. The substrate film was treated by plasma for 10, 20, 30, and 60 seconds, respectively. Grafting yield increased gradually with the reaction period, and the increase was prominent at the first stage of reaction.

The temperature dependence of graft polymerization is shown in Figure 3, where the grafting was made using acrylamide as a monomer in the temperature range from 30°C to 60°C. The yield increased as the temperature increased. Here, the plasma graft polymerization was also carried out with the substrate which was contacted to air for a while after the plasma treatments

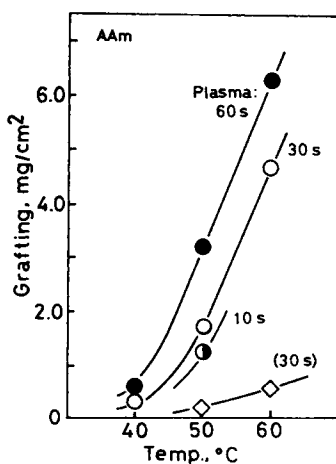


Fig. 3. Temperature dependence of graft polymerization of acrylamide onto porous polypropylene film. (The squares show the results on the substrate films exposed to air after plasma treatment for 30 seconds.)

for 30 seconds. Condition of the residual graft polymerization was quite the same, and the results are given with the squares in the same figure. The yield of graft polymerization by this procedure was found to be much lower, and it suggested that the contact to air reduced the graft polymerization seriously. It has been said that the peroxy radicals ($P-OO\cdot$) were formed from the plasma activated polymer radicals ($P\cdot$) during the contact to oxygen. Then, the thermally produced oxy radicals ($P-O\cdot$) is expected to initiate the graft polymerization, but the initiation effect was not observed so practically in the temperature range investigated for polypropylene.

Graft polymerization is also dependent on the monomer reactivity, and the grafting yield was found to be in the order of acrylamide, acrylic acid and methacrylic acid in these experiments. The lower reactivity of methacrylic acid is probably due to the steric hindrance of the α -methyl group.

Since acrylamide was found to have a higher reactivity in graft polymerization, the copolymerization with sodium styrene-sulfonate (SSNa) was attempted in the various mixture ratios. The copolymerization should be a useful way to incorporate the functional groups into the polymer, such as sulfonate group in the SSNa copolymers. Osada et al.⁵ have reported that plasma copolymerization took place in the mixture of acrylamide and 2-acrylamide-2-methyl-1-propanesulfonic acid which did not graft polymerize by itself. However, when SSNa was used, copolymerization did not proceed practically. As the ratio of SSNa was increased in the total 5% aqueous solution with acrylamide, the grafting yield was seriously lowered, and in the infrared spectra of the products film the absorption peaks which should be derived from poly(SSNa) were not observed. Therefore, it was concluded that the graft polymerization of SSNa did not occur with acrylamide.

During the study of plasma graft polymerization of acrylic acid, acrylamide, and methacrylic acid, it was observed that the viscosity of the monomer solution increased, and the increase was much greater than that carried out with the monomer solution in a reactor where plasma pretreatment was not made. The results observed in the viscosity behavior indicated that homopolymerization took place mainly through the radical transfer to the monomer from the activated radicals by plasma.

Pervaporation

Water-ethanol permseparation through the prepared membranes was investigated by pervaporation. Figure 4 shows the results on the pervaporation through an acrylic acid-grafted membrane (g-AA; grafting yield, 3.53 mg/cm²) and the ionized membrane by sodium hydroxide (g-AA⁻Na⁺). In this figure, flux and the concentration of ethanol in the permeates are plotted against the concentration of ethanol in the feed solutions. Aqueous alcoholic solution up to 90% was used as a feed, and the pervaporation experiments were made at 40°C.

Some characteristic features can be pointed out from the results. First, the ethanol concentration in permeates became lower than that in feed. Secondly, the flux decreased as the concentration in the feed increased. Water permseparation took place in both membranes, and it was much more prominent in the ionized membranes.

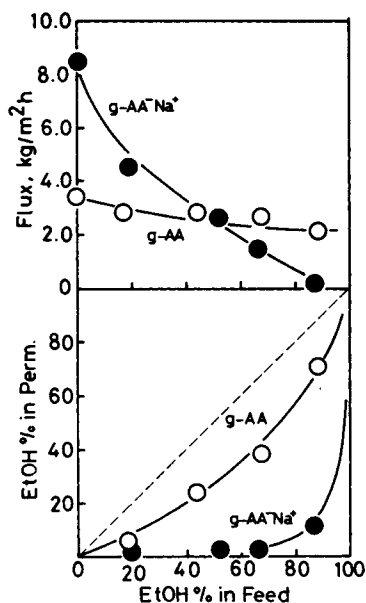


Fig. 4. Results on pervaporation through the acrylic acid grafted membrane (g-AA; grafting, 3.53 mg/cm²) and the ionized membrane (g-AA⁻Na⁺).

The effect of ionization of the grafted layer can be regarded from two aspects; the higher permeation rate in the water-rich feeds, and the higher permselectivity of water throughout the concentration range. When water is used as a feed, the flux exceeds 8.0 kg/m² h in the ionized membranes, which is more than two times greater than that in the un-ionized membranes. (The flux through the ionized membranes is much higher than those through the conventional water-permselective membranes such as poly(vinyl alcohol) and others.) However, as the ethanol concentration in feed increased beyond 60%, the situation was reversed and the flux through the ionized membranes became lower. In other words, the flux decreased prominently in the ionized membranes with the increase of ethanol concentration, while change was much less in the un-ionized membranes.

The higher flux through the un-ionized membranes in the higher concentration range of ethanol was due to the effluence of ethanol as suggested from the results shown in Figures 5(a) and (b), where the portion of ethanol in permeate is plotted against the ethanol concentration in the feed solution and expressed by the shade lines, respectively, for the unionized membrane (a) and the ionized membrane (b). The ethanol portion was calculated from the concentration in the permeates. In the case of the acrylic acid-grafted membrane or the un-ionized membrane, ethanol portion increased gradually with the increase of the concentration in feed, and the main part of flux was occupied by ethanol in the higher concentration range. In contrast, the ethanol portion did not change much, almost remaining constant throughout the ethanol concentration range in the ionized membrane. The results are strongly related to the difference in the permselective behaviors between the two membranes. Thus ionization of membranes is much more effective for the permseparation of water.

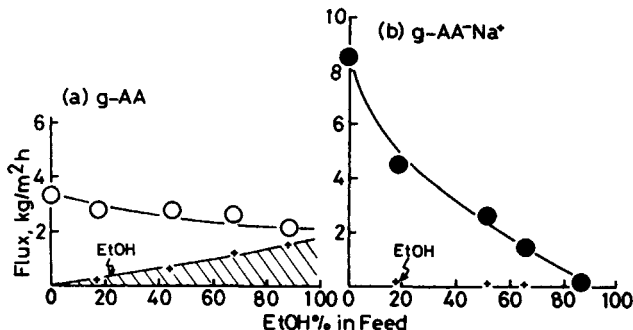


Fig. 5. Portion of ethanol in the permeates for acrylic acid grafted membrane (a) and the ionized membrane (b).

The distinct contrast between the permeation behaviors in both membranes can be explained by the difference in the interaction of $-\text{COO}^-$ group and $-\text{COOH}$ group against the components in the feed solutions; i.e., the $-\text{COO}^-$ group has a much stronger affinity to water but not so much to ethanol, while the $-\text{COOH}$ group has affinity to both.

The permselectivity of these membranes was evaluated by the separation factor of water ($\alpha_{\text{ethanol}}^{\text{water}}$). Figure 6 shows the results for the ionized membranes with various amounts of grafting. (Here, the amount of grafting is given by the weight in neutral state but not in the ionized state of the grafted poly(acrylic acid), and the situation is the same in the following descriptions.) First, the separation factor was dependent on the concentration of ethanol in feed, and the maxima appeared at 60–70% of ethanol. Permselectivity was also dependent on the state of membrane or the amount of the grafted polymer, and the higher permselectivity of water was obtained in the membranes with the graftings of 1.26, 3.16, and 3.53 mg/cm^2 of acrylic acid. Thus, the degree of grafting seems to play an important role for the optimum permseparation of water in the acrylic acid graft-polymerized porous polypropylene films.

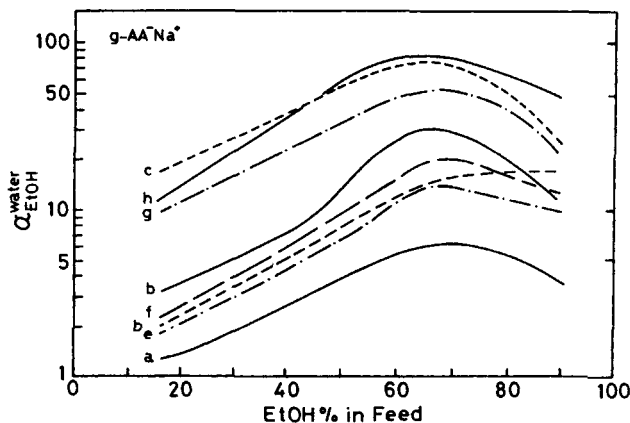


Fig. 6. Separation factor of water ($\alpha_{\text{ethanol}}^{\text{water}}$) obtained through the acrylic acid grafted and then ionized membranes (grafting; 0.61 (a), 0.91 (b), 1.26 (c), 1.61 (d), 2.15 (e), 2.58 (f), 3.16 (g), and 3.53 mg/cm^2 (h)), respectively, at 40°C.

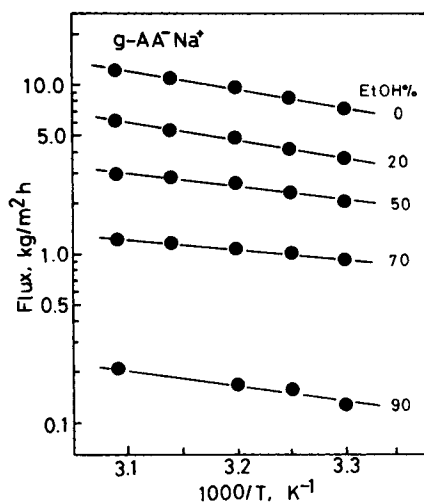


Fig. 7. Arrhenius plots of flux through the ionized membrane (grafting, 1.26 mg/cm²).

Temperature dependence of pervaporation was also investigated with respect to the flux and the separation factor in the temperature range 30–60°C by some membranes with higher permselectivity. Flux increased naturally as the temperature increased. Arrhenius plots were obtained for an ionized membrane (grafting, 1.26 mg/cm²), and is shown in Figure 7 for some concentrations of ethanol. Activation energy for permeation could be obtained from the slope, and some data are summarized in Table I. The activation energy was between 3 and 8 kcal/mole depending on the feed ethanol concentration as well as on the type of membrane. The maximum value in the activation energy appeared to be around 20% of ethanol in the feed solution. It should be noted that the activation energy is generally lower for the ionized membrane whose permselectivity is higher, when the values are compared at the same concentration of ethanol in feed. The activation energy of permeation may have some relation to the permselectivity, but a detailed discussion explaining the relation cannot be given at present.

TABLE I
Activation Energy of Permeation of Water-Ethanol Mixtures
Through the Plasma Graft-Polymerized Membranes

Membrane		Activation energy (kcal/mole)				
Monomer	Grafting (mg/cm ²)	0%	20%	50%	70%	90% ^a
AA ^b	1.26	6.20	8.72	5.66	4.33	4.60
	3.53	5.04	7.38	5.71	5.00	4.41
AA ⁻ Na ⁺ ^c	1.26 ^d	4.85	4.79	3.82	2.45	4.27
	3.53 ^d	5.02	5.56	3.91	3.20	3.07
AAm ^b	1.07	5.24	6.38	6.45	—	—

^a Ethanol % in feed.

^b AA = acrylic acid, AAm = acrylamide.

^c Sodium salt of grafted poly(acrylic acid).

^d Grafting weight before ionization.

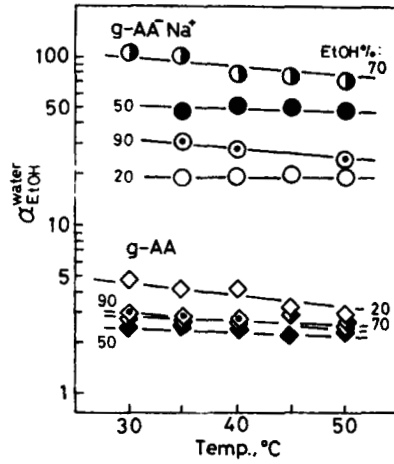


Fig. 8. Temperature dependence of separation factor of water ($\alpha_{\text{EtOH}}^{\text{water}}$) through the acrylic acid grafted membrane and the ionized membrane (grafting, 1.26 mg/cm^2).

Figure 8 shows the temperature dependence of separation factor for the acrylic acid-grafted and the ionized membranes (grafting, 1.26 mg/cm^2). The separation factors are slightly greater in the lower temperature range, and this is related to the lower flux at the region.

Control of grafting on the porous substrate plays an important role on the separation behavior as described previously. At first, in order to have

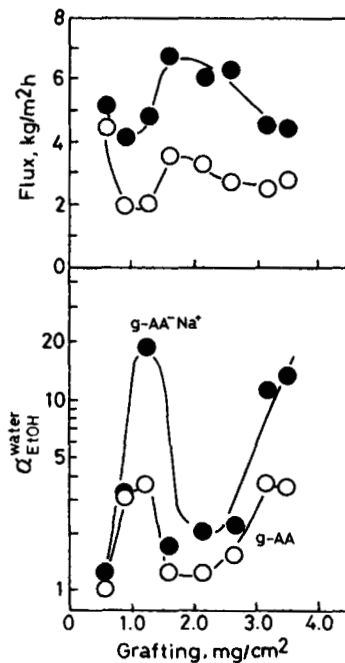


Fig. 9. Dependence of flux and separation factor of water ($\alpha_{\text{EtOH}}^{\text{water}}$) on the grafting weight at ca. 20% of ethanol in feed.

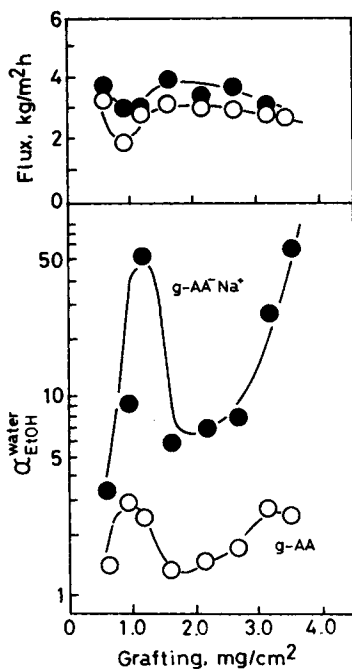


Fig. 10. Dependence of flux and separation factor of water ($\alpha_{\text{ethanol}}^{\text{water}}$) on the grafting weight at ca. 50% of ethanol in feed.

permselectivity the porous membrane must be filled with the grafted polymers to be made nonporous. Dependence of separation on the grafting of membrane was investigated. Figures 9 through 12 show the fluxes and separation factors as a function of the grafting of acrylic acid, respectively, for the ethanol concentrations of 20, 50, 70, and 90% in feeds.

Water-ethanol separation became effective beyond the grafting of about 0.6 mg/cm^2 in both types of membranes. Grafting of 0.6 mg/cm^2 corresponded to about 6 μm in thickness at a rough estimate, and this was much greater than the average pore size of the substrate film. When grafting was smaller than that for filling the pores, the separation did not occur practically and the mixture feed solution was unchanged. An interesting phenomenon was observed in the pervaporation experiments through the membrane in which the pores were just covered with the grafted layer. When the ethanol concentration in feed was lower, permseparation took place, but as the concentration increased, the flux increased suddenly and mixture solution came out. This was probably due to the macropores formed mechanochemically by the aggregation of the thin graft layer in the alcohol-rich feed solutions, which would become the paths of effluent.

The separation factors became maximum and the flux minimum at ca. 1.0 mg/cm^2 of grafting, and then the former decreases and the latter increases generally until 2.0 mg/cm^2 . The separation factor increased again beyond the grafting. Similar phenomena were observed in other types of membranes. The trends were probably ascribed to the state of the grafted membranes.

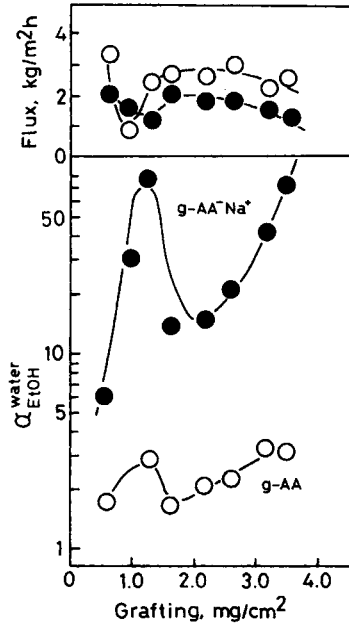


Fig. 11. Dependence of flux and separation factor of water ($\alpha_{\text{ethanol}}^{\text{water}}$) on the grafting weight at ca. 70% of ethanol in feed.

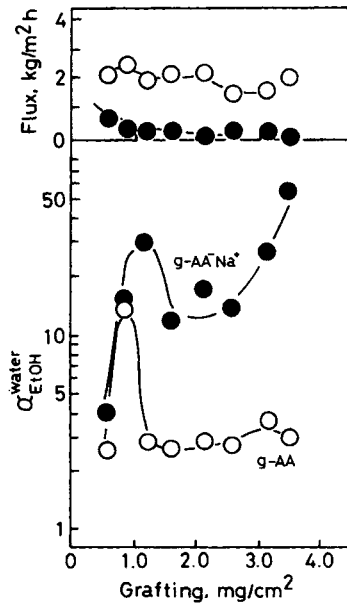


Fig. 12. Dependence of flux and separation factor of water ($\alpha_{\text{ethanol}}^{\text{water}}$) on the grafting weight at ca. 90% of ethanol in feed.

TABLE II
Flux and Separation Factor of Water Through the Membranes

Membrane		Flux (kg/m ² h) ^a					Separation factor ($\alpha_{\text{ethanol}}^{\text{water}}$) ^a			
Monomer	Grafting (mg/cm ²)	0%	20%	50%	70%	90% ^b	20%	50%	70%	90% ^b
AA ^c	1.26	1.55	1.96	2.61	2.36	1.91	3.60	2.45	2.83	2.76
	3.53	3.38	2.82	2.77	2.68	2.10	3.45	2.58	3.15	2.87
AA ⁻ Na ⁺ d	1.26	9.55	4.83	2.66	1.10	0.17	19.3	51.2	79.8	29.7
	3.53 ^e	8.50	4.49	2.63	1.36	0.13	13.5	58.8	78.2	52.1
MAA ^c	1.03	1.49	1.51	0.54	0.88	0.93	3.74	2.24	1.96	2.41
	2.41	1.50	0.37	0.46	1.00	1.06	4.70	2.79	1.86	2.40
MAA ⁻ Na ⁺ d	1.03 ^e	7.17	5.30	3.38	1.82	—	2.01	9.49	28.5	—
	2.41 ^e	7.82	5.49	3.56	1.98	0.45	1.58	7.45	21.7	11.2
AAm ^c	1.27	3.38	3.52	2.77	3.11	—	1.41	2.42	2.36	—
	3.96	3.28	2.64	1.51	0.76	1.10	2.73	7.30	10.9	2.40

^a Measurements at 40°C.

^b Ethanol % in feed.

^c AA = acrylic acid, MAA = methacrylic acid, AAm = acrylamide.

^d Sodium salt of grafted polyacids.

^e Grafting weight before ionization.

Since the plasma treatments are usually surface specific in many polymer substrates, it is expected that the growing of the graft polymers is confined to the surface of the substrate film, and indeed, grafting occurs on just the surface at the first stage of reaction up to around 1.0 mg/cm² of grafting. However, as grafting increased, it was observed that the substrate porous polypropylene film was expanded across the direction of the drawing. This should affect the morphology of the substrate and then the pores. Such marked expansion was found when the grafting exceeded 1.0 mg/cm². It is accordingly thought that the maximum appearing in the water-ethanol separation arises from the filling of pores with the graft polymers in the unexpanded porous film. Expansion of the substrate might result in the decrease of permselectivity due to the decrease in the thickness of the effective permselective layer by grafting. The graft layer became thick enough again for the effective separation of water beyond the grafting of 3.0 mg/cm².

During this study good results in permseparation of water have been achieved by graft-polymerized membranes, although the preparation of membrane was confined to some hydrophilic monomers. Some typical values for flux and separation factor of water are summarized in Table II.

As a matter of fact, the permeation data should be somewhat changeable according to the measurement conditions. The best results were obtained by the acrylic acid-grafted membranes, and the separation factor reached 103 by the ionized membrane (grafting, 1.26 mg/cm²) under the pervaporation conditions at 30°C using the 64.9% aqueous ethanol solution as a feed. As the separation factor increased, the flux usually decreased, and vice versa. Then, for practical use, permselectivity was evaluated by the product of separation factor (α) and flux (Q) (i.e., the value of $\alpha \times Q$). As the best value of $\alpha \times Q$, we have now obtained 150 in the same membrane (48.5 for α and 3.1 kg/m² h for Q) under the pervaporation conditions at 50°C with using the 48.5%

aqueous ethanol solution as a feed. The values for pervaporation should be made higher through the improvement of the membranes.

CONCLUSION

Important aspects described here may be summarized as follows:

1. Permsepation of water is possible through the plasma graft-polymerized membranes, in which nonporous structure is constructed with hydrophilic polymers on porous film.
2. Great hydrophilic and resultingly great permselective layers can be obtained by ionization of the graft layer.
3. Graft layers are stable and insoluble even in the ionized state because they are bonded covalently to the substrate films.
4. Mechanical stability, which is important for practical use, is owing to the substrate film. Namely, the roles of permsepation and mechanical strength are shared to the graft layer and the substrate porous film, respectively, in the permselective membranes.

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References

1. I. Cabasso and Z-Z. Liu, *J. Membrane Sci.*, **24**, 101 (1985).
2. A. Wenzlaff, K. W. Böddeker, and K. Hattenbach, *J. Membrane Sci.*, **22**, 333 (1985).
3. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *Polymer Preprint, Japan*, **34** (3), 401 (1985).
4. S. M. Suchecki, *Textile Indu.*, March, (1975) 91.
5. Y. Osada, Y. Iriyama, and M. Ohta, *Nippon Kagaku Kaishi*, (1983) 831.
6. S. Yamada, *Maku(Membrane)*, **6**, 168 (1981).

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