

Pervaporation of Ethanol–Water Mixture by Co⁶⁰ γ -Ray Irradiation-Modified Nylon 4 Membrane

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SYNOPSIS

The ethanol–water separation by pervaporation with γ -ray irradiation-modified nylon 4 membrane was investigated. The membrane was prepared by homografting γ -ray irradiation of vinyl acetate (VAc) monomer onto nylon 4, poly(vinyl acetate) (PVAc)-homo-*g*-nylon 4 followed by hydrolysis treatment, poly(vinyl alcohol) (PVA)-homo-*g*-nylon 4. The homografting method shows significant improvement in the degree of grafting of (VAc) onto nylon 4 over the heterografting method. For example, the degrees of grafting of the VAc with 30 vol % and total dose of 2 Mrad for the heterografted method and for the homografted method are 14.1 and 42.2%, respectively. The effects of irradiation with or without oxygen in solution, irradiation time, VAc content, degree of grafting, crystallinity, feed concentration, and operating temperature on performances of the PVA-homo-*g*-nylon 4 membrane were carried out. Comparison of the separation factor of sorption in membrane (α_{sorp}) and that of pervaporation (α_{perv}) was made. A separation factor of 7.3 and a 0.691 kg/m² h permeation rate can be obtained by the PVA-homo-*g*-nylon 4 membrane with a degree of grafting of 42.2% for 90 wt % ethanol feed concentration. Compared with the unmodified nylon 4 membrane, which has the separation factor of 4 and permeation rate of 0.350 kg/m² h, the PVA-homo-*g*-nylon 4 membrane shows improved a separation factor and permeation rate. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The separation process by pervaporation through graft polymerization of some vinyl monomers onto the polymeric substrate has been investigated.^{1–6} The various modified methods included were blending, cross-linking,^{7–10} and copolymerization.^{11,12} This process is potentially useful in fields where pervaporation techniques are appropriate, such as fractionation of close-boiling components, azeotropic mixtures, isomeric mixtures, and heat-sensitive mixtures.

The mechanism of the separation process of binary mixtures is complicated because of the difference in affinities of the permeating mixture for the polymer membrane. The diffusion coefficients of the components are used principally to separate them, thus resulting in nonlinear transport with respect

to the permeant concentration.^{13–19} Thus, specific and selective separation of substances through membranes may be realized by incorporating a function group into the membrane that may result in a strong interaction such as hydrogen bonding, coulombic interaction, and electron donor–acceptor interaction. It is expected that hydroxy groups might have a strong interaction with water in aqueous solution through hydrogen bonding. Therefore, in the pervaporation process, the hydrogen bonding between the membrane material and water plays an important role in enhancing the permselectivity of water.^{1,9,20,21} One component of the feed mixture may be preferentially absorbed into the membrane and the strong interaction of the functional group increases the permselectivity. Yoshikawa et al.^{12,22} reported that introducing imide groups into the membrane structure can be very effective in enhancing the selectivity of the membrane for water. Poly(vinyl alcohol) (PVA) is highly hydrophilic and has excellent selectivity toward water for dehydrating aqueous ethanol solution.²¹ This feature can be

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used to improve the hydrophilicity of polyamide membrane for the pervaporation process, if the stability of PVA in solution can be overcome.

To improve the instability of PVA in water, membranes are usually modified by chemical grafting, γ -ray irradiation grafting, or heat treatment.²³⁻²⁵ Nylon 4 membrane has been regarded as a promising membrane material for separation purposes because of its excellent strength and inherent affinity to water. Use of Co^{60} γ -ray irradiation, chemical grafting, and plasma deposition methods to improve the performance of nylon 4 for reverse osmosis,²⁶ ultrafiltration,²⁷ dialysis,²⁸ and hemodialysis²⁹ have been reported by our laboratory. To improve the hydrophilicity of nylon 4 membranes for pervaporation purposes and to overcome the dissolution of PVA in water, this study attempts to obtain PVA-homo-g-nylon 4 membrane by γ -ray irradiation homografting of vinyl acetate (VAc) onto nylon 4 membrane, followed by hydrolysis treatment. The effects of VAc content, irradiation time, irradiation with or without oxygen, degree of grafting, crystallinity, feed concentration, and operating temperature on the performance of PVA-homo-g-nylon 4 membranes were studied. The comparison of separation factors of sorption in membrane (α_{sorp}) and pervaporation (α_{perv}) was also discussed.

EXPERIMENTAL

Material

Nylon 4 was synthesized as described previously.²⁶ Molecular weights of nylon 4 measured by a Cannon-Fenske viscometer with *m*-cresol as a solvent at 25°C are 20,000–22,000. Formic acid and normal propyl alcohol supplied by Nihon Shiyaku Industries Co. were used as medium and casting solvents. VAc was supplied by Merck Co. and separated from the hydroquinone stabilizer by vacuum distillation. The distilled monomer was stored in a brown glass bottle at –10°C.

Homograft Copolymerization

Nylon 4 was placed in a 250 mL flask, in which the medium solvent was added. After nylon 4 was thoroughly dissolved, VAc monomer was added to the flask. The final total amount of solution was 100 mL. The flask was degassed by three freeze-pump-thaw cycles and sealed off under high vacuum. The solution with dissolved oxygen was also considered. The graft copolymerization was carried out by uti-

lizing a high-energy Co^{60} γ -ray irradiation method. The irradiation rate was 0.1 Mrad/h. After the irradiation, the reaction solution was poured into an excess of cold methanol and then the crude graft product was kept in a Soxhlet apparatus for more than 48 h to extract poly(vinyl acetate) (PVAc) homopolymer with acetone. Then, the precipitate was dried and weighed. The degree of grafting was calculated according to the following equation:

Degree of grafting (D.G.)

$$= \frac{\text{weight of grafted nylon 4} - \text{weight of nylon 4}}{\text{weight of nylon 4}}$$

Membrane Preparation

The membrane of PVA-homo-g-nylon 4 was prepared from a casting solution of grafted copolymer in the formic acid/*n*-propyl alcohol mixed solvent. The polymer concentration in the casting solution was 10 wt %. The membrane was formed by casting the solution on a glass plate to a predetermined thickness. The glass plate was then heated at 70°C for 40 min. The membrane peeling off from the glass plate was hydrolyzed by a 0.5N NaOH solution at room temperature for 2 h and afterward washed with distilled water. The membrane with an average thickness of $25 \pm 2 \mu\text{m}$ was stored in various concentrations of ethanol aqueous solution for at least 12 h before subsequent usage.

Apparatus and Measurements

A normal vacuum pervaporation apparatus consisted of a cell made of stainless steel with circulation of the liquid over the membrane. The membrane area in contact with the feed solution was 10.2 cm². The membrane was supported by filter paper resting on a sintered stainless steel disk. A vacuum pump maintained the downstream pressure at 3–5 mmHg, and the permeate was collected in a trap cooled by liquid nitrogen and analyzed by gas chromatography (GC, China Chromatography 8700T). The permeation rate was determined by the weight of the permeate. The separation factor was calculated from the following equation:

Separation factor

$$= (Y_{\text{water}}/Y_{\text{alcohol}})/(X_{\text{water}}/X_{\text{alcohol}})$$

where *X* is the feed concentration, and *Y*, the permeate concentration. FTIR spectra were obtained at 4 cm⁻¹ resolution using a Bomem MB-100 FTIR.

A Shimadzu XD-5 XRD diffractometer was used employing $\text{CuK}\alpha$ radiation at the following parameters: accelerating voltage 30 kV and anodic current 20 MA. Diffractograms were made by continuous scanning over the range of diffraction angle 2θ from 5° to 35° at a rate of $4^\circ/\text{min}$. Thermogravimetric analyses (TGA) were obtained on a DuPont TGA-951 at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Degree of Swelling and Sorption Measurement

The clean and dried membranes with known weights were immersed in ethanol feed concentration at room temperature for 24 h to reach equilibrium swelling. These pieces were rapidly removed from the bottle, blotted to remove the surface solvent, and placed on a weighting scale. The first reading was taken 40 s following removal of the membrane from the mixture, and four to five readings were made at 10 s intervals. The weight of the solvent-swollen membrane was obtained by extrapolating the initial portion of the experimental curve to zero line.³⁰ The degree of swelling was calculated by the following equation:

Degree of swelling

$$= \frac{\text{weight of swollen nylon 4} - \text{weight of nylon 4}}{\text{weight of nylon 4}}$$

where the weight of nylon 4 and the weight of swollen nylon 4 denote the weight of dry and solvent-swollen membranes, respectively. The PVA-homog-nylon 4 membrane was allowed to equilibrate in mixtures of the various concentration of ethanol aqueous at 25°C . The swollen membranes were removed from the mixture solution, and the surface solution was blotted. The substances in the swollen membranes were then desorbed under reduced pressure and collected in traps immersed in liquid nitrogen. The composition of sorption in the membrane, determined by gas chromatography and used to calculate the separation factor, was defined as

$$\alpha_{\text{sorp}} = \frac{S_{\text{water}}/S_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}}$$

where $S_{\text{water}}/S_{\text{ethanol}}$ and $X_{\text{water}}/X_{\text{ethanol}}$ denote the concentration ratio of the substances in the membrane and feed solution, respectively.³¹

RESULTS AND DISCUSSION

Effect of the Oxygen on the Degree of Grafting

As shown in Figure 1, under the same irradiation dose, the degree of grafting with dissolved oxygen is lower than that without. During Co^{60} γ -ray irradiation grafting in the presence of oxygen, diperoxide, or hydroperoxide, compounds may be produced and become resistant to the grafting.^{32,33} Therefore, the degree of grafting with dissolved oxygen is lower than that without. It is observed that, with an increase in VAc monomer concentration, the degree of grafting increases and reaches a maximum at 30 vol % and then falls off. This phenomenon is probably due to the increase in viscosity of the polymerization solution and to the decrease of the polymer chains of the polymerization reaction. It is indicated that the gel effect was more pronounced at higher concentration of the VAc monomer. The results from this study suggested that the graft polymerization reaction should not exceed 30% VAc concentration in the absence of oxygen.

Effect of the VAc Content and the Total Dose on the Degree of Grafting

An attempt was made to improve the low degree of grafting of VAc on nylon 4 with the heterografting

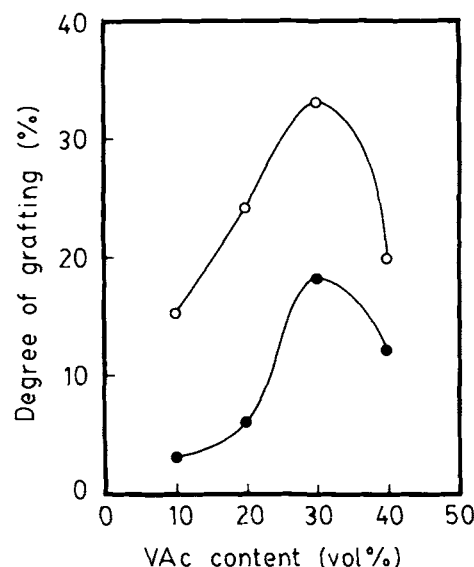


Figure 1 Effect of oxygen in grafting solution on the degree of VAc monomer grafted onto nylon 4: irradiation time 10 h; dose rate 0.1 Mrad/h; medium solvent: formic acid : *n*-propanol = 4 : 1 vol %; solution condition: (○) without dissolved O₂; (●) with dissolved O₂.

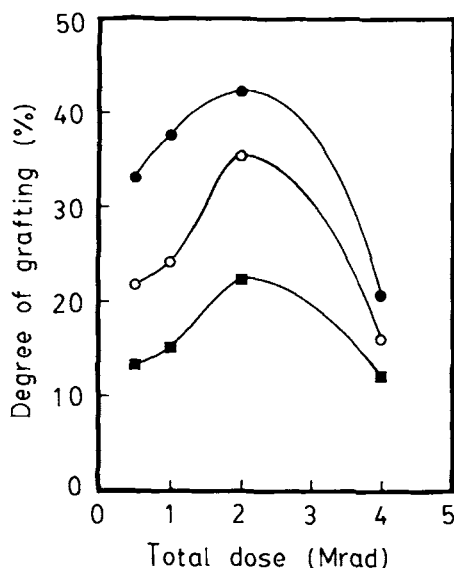


Figure 2 Effect of total dose on the degree of VAc monomer grafting onto nylon 4; dose rate 0.1 Mrad/h; solution condition: without dissolved O_2 ; (●) VAc monomer concentration: 30 vol %; (○) 20 vol %; (■) 10 vol %.

method. For example, the degree of grafting of the VAc with 30 vol % and total dose 2 Mrad is 14.1%. In this study, the graft polymerization reaction was carried out by γ -ray irradiation-induced VAc aqueous at constant dose rate of 0.1 Mrad/h for various time periods. Figure 2 shows that when the total dose exceeds a certain limit (2 Mrad) the degree of grafting begins to decrease. For example, the degree of grafting of the 30 vol % VAc content, total dose 2 Mrad, is 42.2%. At the beginning of irradiation, the degree of grafting increased due to the increased active sites and then the degradation of PVAc occurred after sufficient energy was irradiated; hence, the degree of grafting decreased. This tendency of homografting was similar to that of het-

Table I FTIR Spectra with Relative Absorbance on VAc Homografted Nylon 4 Membranes with Various VAc Concentrations

VAc Monomer Concentration (Vol %)	Total Dose (Mrad)	Degree of Grafting (%)	Relative Absorbance A_{1738}/A_{1475}
10	2	22.4	2.33
20	2	35.4	4.68
30	2	42.2	5.48
40	2	38.0	5.01

Dose rate: 0.1 Mrad/h.

erografting.³⁴ It was also observed that the degree of grafting increases as VAc content increases. Additionally, the relative absorbance A_{1738}/A_{1475} was evaluated by measuring the ratio of (C=O) absorbance at 1738 cm^{-1} (A_{1738}) to the $\delta_s(-\text{CH}_2-)$ band absorbance at 1475 cm^{-1} (A_{1475}). The absorbance of the 1475 cm^{-1} ($-\text{CH}_2-$) group was kept at almost the same level for every spectra and used as a reference because it was independent of the degree of grafting. Table I shows that the relative absorbance increases as the VAc monomer concentration increases up to 30 vol %, which reaches to a maximum value ($A_{1738}/A_{1475} = 5.48$) and then decreases in the range 10–40 vol % at a constant total

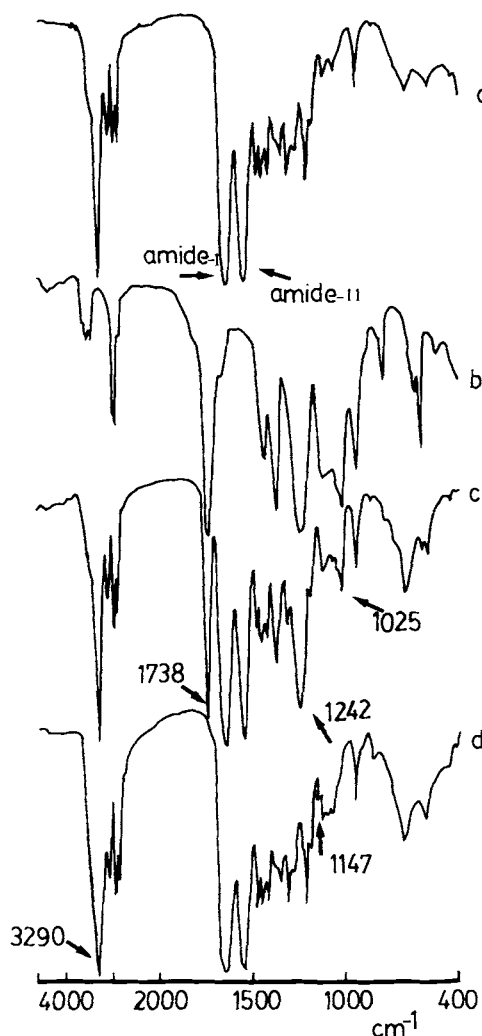
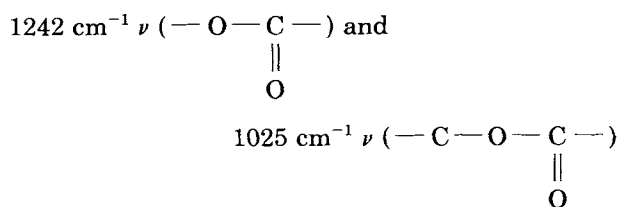


Figure 3 (a) FTIR spectra of ungrafted nylon 4 membrane; (b) PVAc homopolymer; (c) PVAc-homo-*g*-nylon 4 membrane with degree of grafting 42.2%; (d) PVAc-homo-*g*-nylon 4 membrane with degree of grafting 42.2% after hydrolysis treatment.

dose. This observation agrees with that shown in Figure 1. It was suggested from this experiment that total dose should not exceed 2 Mrad for good membrane formation.

Characterization of Grafting Polymer

The FTIR spectra of ungrafted polymer (a), PVAc homopolymer (b), PVAc-homo-*g*-nylon 4 membrane with degree of grafting 42.2% (c), and hydrolysis with 0.5*N* NaOH (PVA-homo-*g*-nylon 4) (d), are shown in Figure 3. The PVAc-homo-*g*-nylon 4 membrane shows a sharp peak at 1738 cm⁻¹ (typical of C=O vibrations),



due to the VAc that is not found in unmodified nylon 4 membrane (spectra a) in the range 4600–400 cm⁻¹.³⁵ It indicated that the PVAc-homo-*g*-nylon 4 graft polymer was synthesized. Spectra (d) of Figure 3 shows that the absorbance at 1738 cm⁻¹ disappears and the absorbance at 3290 cm⁻¹ becomes much broader after 2 h of hydrolysis. This result suggests that the ester group of PVAc is completely hydrolyzed.³⁸ Furthermore, from Table II, the degree of hydrolysis increases with time and the relative absorbance (A_{1738}/A_{1475}) decreases with time. These results confirmed that the VAc monomer was already grafted onto the membrane structure.

Effect of Degree of Grafting on Pervaporation Performances

The pervaporation testing was carried out with 90 wt % ethanol feed concentration through the membrane with different degrees of grafting. As shown in Figure 4, the permeation rate increases and the separation factor reaches a maximum $\alpha = 11$ and then decreases as the degree of grafting increases. This may be due to the hydroxy group in the membrane increasing as the degree of grafting increases. X-ray diffraction studies revealed the structure transition in the grafted membrane with various degrees of grafting, as shown in Table III.

Determination of the amorphous curve was made by adaption of procedures reported by the Weidinger-Hermans method.^{36,37} The X-ray diffraction diagram of the grafted polymer showed that the intensity of the diffraction at angles $2\theta = 20.5^\circ$ and $2\theta = 24^\circ$ decreases with increasing the degree of grafting, resulting in the crystallinity decrease. A higher degree of grafting results in a relaxation structure of the PVA-homo-*g*-nylon 4 membrane. Thus, as the hydroxy group increases, the crystallinity decreases at the higher degree of grafting, resulting in an increase in the permeation rate. For example, the permeation rates for the membrane with 42.2% degree of grafting and for the unmodified membrane are 0.691 and 0.350 kg/m² h, respectively. However, for higher than a 13.4% degree of grafting, the permselectivity will be decreased. This could be explained by the fact that the PVA possesses higher hydrophilicity and lower crystallinity. Additionally, the data of the thermal characterization of the PVA-homo-*g*-nylon 4 membrane with various degrees of grafting are also listed in Table III. The temperature of the start intense degradation (T_{start}) decreases with increasing the degree of grafting. The higher

Table II Degree of Hydrolysis of the Nylon 4 Homografted VAc Membrane with Degree of Grafting 42.2% in Different Hydrolysis Times

Hydrolysis Time (Min)	Relative Absorbance	
	A_{1738}/A_{1475}	Degree of Hydrolysis
0	5.48	0.00
20	4.26	0.22
40	2.06	0.62
60	1.01	0.82
90	0.28	0.95
120	0.00	1.00

Hydrolysis condition: 0.5*N* sodium hydroxide solution.

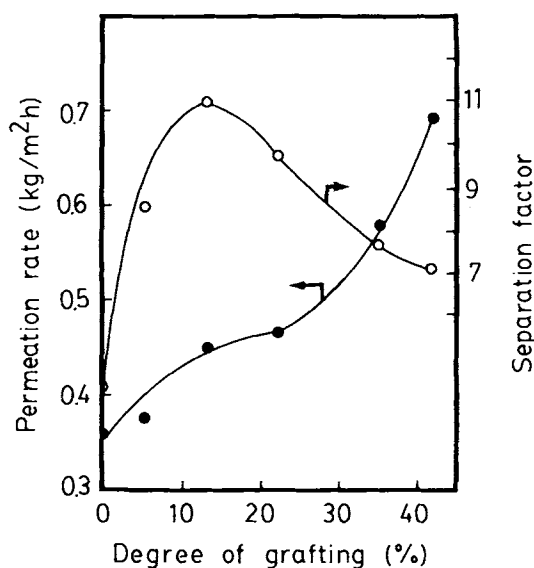


Figure 4 Effect of degree of grafting on permeation rate and separation factor through PVA-homo-*g*-nylon 4 membrane cast from polymer solution without dissolved oxygen; operation condition: 90 wt % ethanol feed concentration; 25°C; downstream pressure 3 mmHg; thickness 25 μ m.

degree of grafting seems to result in a relaxation structure of the PVA-homo-*g*-Nylon 4 membrane.

This phenomenon was the same as that mentioned in the crystallinity measurement. In the previous paper,³⁴ we found that the membrane by γ -ray heterografting VAc onto nylon 4 has a 0.352 kg/m² h permeation rate at 21.2% degree of grafting. Nevertheless, the PVA-homo-*g*-nylon 4 membrane offers an even higher permeation rate of 0.465 kg/m² h at the same degree of grafting, because the

Table III Measurements of Degree of Crystallinity of PVA-Homografted-Nylon 4 Membrane with Various Degrees of Graft Obtained by the Method of Hermans and Weidinger

Degree of Grafting (%)	F Area ^a (mm ²)	H Segment ^b (cm)	Degree of Crystallinity (%)	T_{start}^c (°C)
13.4	87	4.1	14.1	296.9
22.4	86	4.2	13.3	294.7
35.4	78	4.1	13.2	290.1
42.2	73	4.2	12.5	276.9

^a F: The area of the plot between the diffraction curve and background curve corresponding to radiation diffracted by crystalline regions.

^b H: The height of background diffuse scattering.

^c T_{start} : The temperature of the start of intense degradation at the heating rate of 20°C/min.

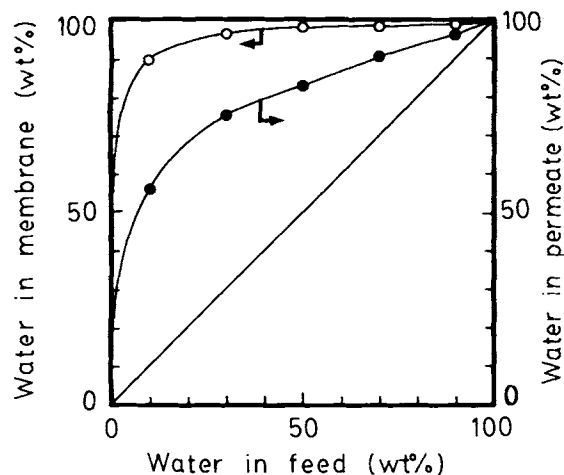


Figure 5 Water concentration in membrane and in permeates of PVA-homo-*g*-nylon 4 membrane with degree of grafting 13.4% as a function of feed concentration at 25°C.

hydroxy group in the latter seems to relatively more easily loosen the nylon 4 structure. From this result, it may be manifested that the homografting modification technique is a very useful tool to improve the permeation rate.³⁸

Sorption of Binary Liquid Mixture

According to the solution-diffusion model, the effects of solubility and diffusivity play an important role in the membrane permselectivity.³⁰ Thus, sorption experiments for the grafted polymer were conducted. Figure 5 shows the effect of the feed water concentration on the water concentration in permeate and in the membrane for the PVA-homo-*g*-nylon 4 membrane. The permeate and sorption composition curves lie above the diagonal, indicating that the PVA-homo-*g*-nylon 4 membrane allows water to permeate in preference to ethanol. Additionally, it shows that the water concentration of the sorption in the membrane is higher than that of the permeate through the membrane. Thus, the separation factor of sorption (α_{sorp}) is higher than that of the pervaporation (α_{perv}). This phenomenon might be due to higher water affinity of the hydroxy group in the membrane. It is suggested that the water molecules are selectively dissolved into the PVA-homo-*g*-nylon 4 membrane that possesses hydrophilic hydroxy and amide groups and most of those molecules are, thus, diffused through the membranes. Table IV shows the total and preferential sorption of various concentrations of ethanol aqueous in PVA-homo-*g*-nylon 4 membrane with degree of grafting of 42.2%. The total sorption in-

Table IV Overall and Preferential Sorption of Various Ethanol Mixtures in PVA-Homo-*g*-Nylon 4 Membrane with Degree of Grafting 42.4%

Feed (%)	Total Sorption (g/g)	Water Sorption (g/g)	Ethanol Sorption (g/g)	α_{sorp}	α_{perv}
10	1.466	1.452	0.014	10.0	2.0
30	1.355	1.342	0.013	42.9	3.7
50	1.335	1.313	0.023	57.1	4.5
70	1.271	1.218	0.053	53.7	5.1
90	1.255	1.070	0.184	52.3	7.3

creases as the ethanol feed concentration increases from 90 to 10 wt %.

Considering the individual components, it can be seen that the amounts of absorbed ethanol changed monotonically with a change in the weight fraction of water in the feed solution, resulting in a strong increase in sorption selectivity or preferential sorptions. Comparison of the preferential sorption and the pervaporation shows that it is apparent that the water is absorbed and permeated preferentially. In other words, thermodynamic interaction or preferential sorption is the predominating step in the selective transport.³⁹

Effect of the Feed Concentration on Pervaporation Performances

Figure 6 shows the effects of feed ethanol concentration on the degree of swelling through the grafted polymer with various degrees of grafting. The degree

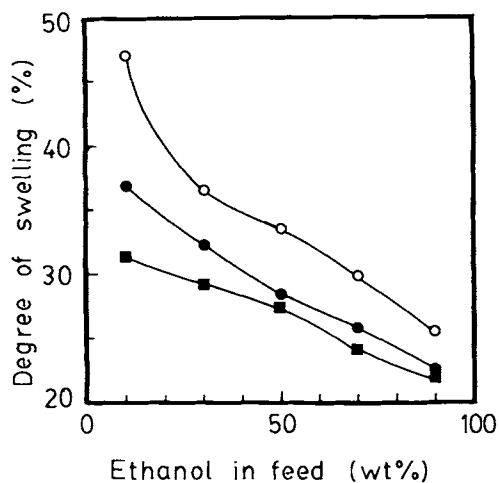


Figure 6 Effect of feed ethanol concentration on degree of swelling: (○) PVA-homo-*g*-nylon 4 membrane with degree of grafting 42.4%; (●) PVA-homo-*g*-nylon 4 membrane with degree of grafting 13.4%; (■) unmodified nylon 4 membrane.

of swelling increases with decreasing ethanol concentration in the feed mixture. At all feed compositions, the degree of swelling of the PVA-homo-*g*-nylon 4 membrane with a degree of grafting of 42.2% is much higher than that of the PVA-homo-*g*-nylon 4 membrane with a degree of grafting of 13.4% and an unmodified membrane. This might be because the interaction between the hydroxy group and the water molecule of the feed solution increases with increasing water content in the feed solution. Furthermore, Table III shows that the crystallinity decreases with increasing the degree of grafting of the PVA-homo-*g*-nylon 4 membrane, resulting from loosening in the structure of the membrane. These results confirm the above swelling effect. This tendency was similar to that of the individual components of water sorption into the membrane (Table IV). The effects of ethanol concentration in the feed solution on the separation factor and permeation rate are shown in Figure 7. The separation factor sharply increases with increasing the ethanol feed concentration. Both the total permeation rate and the partial permeation rate of water decrease with an increase in ethanol concentration, whereas the partial permeation rate of ethanol increases with linear relationships. It reflects the concentration dependence of diffusivity in this system.

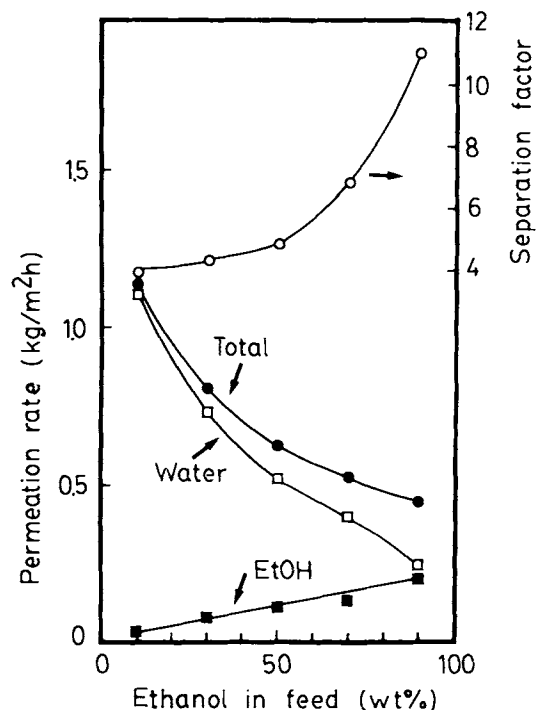


Figure 7 Separation factor and permeation rate values as function of feed ethanol concentration through PVA-homo-*g*-nylon 4 membrane with degree of grafting 13.4%.

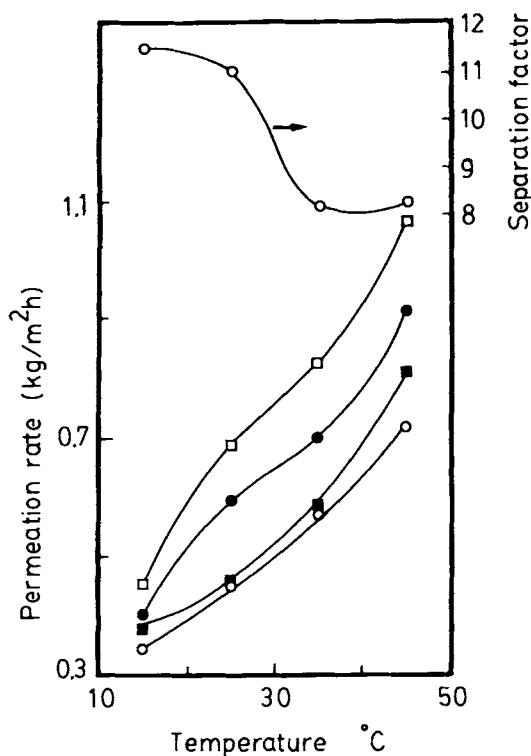


Figure 8 Dependence of separation factor and permeation rate on temperature PVA-homo-*g*-nylon 4 membrane with various degrees of grafting (D.G.) at 90% ethanol concentration in the feed: (○) D.G. = 13.4%; (■) D.G. = 22.4%; (●) D.G. = 30.4%; (□) D.G. = 42.2%.

These results imply that the diffusivity of ethanol through the grafted polymer depends slightly on the concentration because of its low affinity to the grafted polymer. However, water shows a relatively large concentration dependence. This is attributable to water swelling of PVA-homo-*g*-nylon 4 membrane with a 13.4% degree of grafting. Clearly, this increase in the partial permeation rate of water results in the decrease in the separation factor at lower ethanol concentration feeds.

Effect of Temperature

The effect of temperature on permeation rate and separation factor, using a 90 wt % ethanol feed concentration at 3 mmHg downstream pressure, is presented in Figure 8. The permeation rate was found to increase from 15 to 45°C, whereas the separation factor decreased. From these phenomena it may be assumed that the increases of swelling of the membrane matrix at higher temperature results in increased polymer segmental motions. This facilitates the transport of ethanol molecules along with water, thus reducing the separation factor. An assumption is made that the Arrhenius law is valid for a pervaporation of the mixture. The variation of permeation rate for given feed concentration as a function of the reciprocal of the absolute temperature is generally linear, and an apparent activation energy can be drawn from the slope of the plots, as shown in Table V. It has been observed that the activation energy of PVA-homo-*g*-nylon 4 membrane became generally smaller than that of the PVA-hetero-*g*-nylon 4 membrane. The decrease of activation energy was also observed in the pervaporation through the homografted membrane with various degree of grafting, but the change was much smaller.

The activation energy of PVA-homo-*g*-nylon 4 membrane and PVA-hetero-*g*-nylon 4 membrane lay in the range of 5.8–7.4 and 6.7–7.9 kcal/mol, respectively. The lower activation energy of the homografted polymer for the ethanol–water feed solution could be explained as that the PVA-homo-*g*-nylon 4 membrane has higher hydrophilicity than that of PVA-hetero-*g*-nylon 4 membrane.

CONCLUSIONS

We have investigated various ways, such as plasma deposition and heterografting of γ -ray irradiation,

Table V Activation Energy of Permeation by Pervaporation Obtained from the Arrhenius Plots

Membrane	Degree of Grafting (%)	Activation Energy (kcal/mol)				
		90 Wt %	70 Wt %	50 Wt %	30 Wt %	10 Wt %
Heterografted	0.0	7.6	6.9	7.2	6.9	6.2
	12.3	6.8	6.7	7.4	6.5	6.5
	21.2	7.1	6.9	6.7	7.9	6.4
Homografted	13.4	5.8	5.8	6.9	7.4	6.6
	22.4	6.4	6.9	6.9	6.9	6.8
	42.2	6.2	6.6	6.7	7.0	5.9

to improve the membrane morphology and the pervaporation performances of the nylon 4 membrane. The key factors affecting the pervaporation performance include the crystallinity of the membrane, feed solution temperature, and interaction between the hydroxy group in the membrane and the feed solution. Throughout this study, we have established a new method (homografting) of modified nylon 4 membranes for ethanol dehydration. The homografting method significantly improves the degree of grafting of VAc onto nylon 4 compared with the heterografting method. The degree of grafting with dissolved oxygen is lower than that without oxygen. The crystallinity of the membrane and T_{start} decrease with increasing the degree of grafting, resulting in the permeation rate increases. The permeation rate and the separation factor of PVA-homo-*g*-nylon 4 membrane are higher than that of the unmodified nylon 4 membrane in all ranges of feed composition. The activation energy is generally lower than that of the PVA-hetero-*g*-nylon 4 membrane in the operation temperature range of 15–45°C, which is ascribed to the higher hydroxy group content in the PVA-homo-*g*-nylon 4 membrane.

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