Formation of Multilayer Poly(acrylic acid)/Poly(vinylidene fluoride) Composite Membranes for Pervaporation

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ABSTRACT: Dual- and multilayer composite membranes, consisting of poly(acrylic acid) (PAA) and poly(vinylidene fluoride) (PVDF), were synthesized by the plasma-induced polymerization technique. The dual-layer membrane had a dense PAA layer grafted onto a microporous PVDF substrate, whereas in the multilayer membranes, the grafted PAA and the PVDF layers were arranged in an alternating sequence (e.g., PAA/PVDF/PAA and PAA/PVDF/PAA/PVDF/PAA). These membranes were used in a pervaporation process to separate ethanol–water solutions. For the dual-layer membranes, the results indicated that the separation factor increased and the permeation flux decreased with increasing amounts of grafted PAA. For the case of grafting yield < 0.6 mg/cm^2, the composite membrane demonstrated poor separation. As the grafting yield reached 0.85 mg/cm^2, a sharp increase of the separation factor was observed. For the multilayer membranes, the pervaporation performances were very good, with high separation factors (on the order of 100) and reasonable permeation fluxes over a wide ethanol concentration range. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2266–2274, 2004

Key words: membranes; plasma polymerization; poly(vinylidene fluoride) (PVDF); pervaporation; separation of polymers

INTRODUCTION

Pervaporation is a membrane-separation process that has been commercialized for many years as an energy saving, cost effective, and environment-protecting unit operation that can compensate for the distillation process in a number of applications, for example, where a high-temperature condition is prohibited (such as heat-sensitive product from fermentation) or where azeotrope solutions are the targets of separation.[1–16] In a typical pervaporation process, the feed solution contacts a permselective membrane in the upstream side, whereas in the downstream side evacuation is applied as the driving force for feed molecules to transport through the membrane. The permeate, in the form of a gas, is then collected by condensation through a cold trap. Separation of the feed is made possible by the membrane that offers different selectivity toward various species in the feed solution. It is generally accepted that the feed molecules have to first dissolve (sometimes termed "sorption" in the membrane pervaporation literature) into and then diffuse across the dense permselective layer before they depart the membrane. Into this context, any parameters that affect the solubility and the diffusivity of the feed molecules play a role on the performance of the pervaporation process. Clearly, dissolution is associated with molecular interactions among feed molecules and polymer, which can be described by Flory–Huggins theory that involves the interaction parameters. The diffusion process on the other hand depends on the available free volume for migration, which is strongly influenced by the degree of plasticization of the polymer caused by swelling.

Over the years, many kinds of pervaporation membranes have been developed to fulfill specific needs, which can be categorized in terms of microstructure (e.g., asymmetric, uniform), geometry (e.g., cylindrical, flat sheets), and physical property (e.g., hydrophobic, hydrophilic), for example.[5–16] In the present research, we prepared a novel composite membrane, which had a multiple-layer configuration composed of poly(acrylic acid)/poly(vinylidene fluoride) (PAA/PVDF) structural units arranged in an alternating PAA/PVDF/PAA/··· sequence. The hydrophilic PAA layers were known to be effective for separation of alcohol/water solutions, whereas the PVDF layers, which were porous and mechanically strong, functioned as mechanical supports. In other words, the composite membrane owned many active permselective layers separated by porous supports. The membranes were tested over the entire composition range of ethanol/water mixtures and the results indicated a significant improvement of the pervaporation perfor-

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mance over conventional membrane that had only one permselective layer.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (Hylar 5000 HP, specific gravity = 1.75, melt viscosity = 18.7 kpoise; Ausimont USA Inc., Thorofare, NJ) was a semicrystalline polymer. *N*-Methyl-2-pyrrolidone (NMP, 99%, d = 1.028 g/mL; Acros Organics, Morris Plains, NJ) and water (distilled and deionized) were used, respectively, as the solvent and nonsolvent for the polymer. Acrylic acid (99.5%, d = 1.0510 g/mL; Acros) was vacuum distilled to remove trace of inhibitor [methyl ether of hydroquinone (MEHQ)] before grafting it onto PVDF membranes. Ethanol (99.5%, d = 0.79 g/mL; Aldrich, Milwaukee, WI) was used to make aqueous solutions for pervaporation experiments.

PVDF membrane substrate formation

Porous PVDF membranes, used as the substrate for the preparation of PAA/PVDF composite membranes, were prepared by the immersion–precipitation method. In brief, a dope composed of 20 wt % PVDF in NMP was cast onto a glass plate and then immersed in a 70 wt % NMP aqueous solution to induce precipitation. The nascent membrane was washed in a series of nonsolvents and then dried at 45°C. The morphology of the membrane was observed by means of SEM.

PAA/PVDF composite membrane formation

PAA was covalently grafted onto the surface of the PVDF membrane by plasma-induced free-radial polymerization. The membrane was plasma-irradiated (50 W, argon at 0.4 Torr) for 1 min and then exposed to the air for 10 min to form peroxide on the membrane surface. Then it was immersed directly in a deaerated PAA/water solution containing 0.0015*M* Mohr's salt at 80°C for a specific period of time.[17] The grafted composite membrane was washed with water to remove residual ungrafted AA and PAA. The presence of PAA on the PVDF membrane was identified by FTIR/ATR (Magna-IR spectrometer 550; Nicolet Analytical Instruments, Madison, WI) at the absorption peak of the carbonyl group (1710 cm^{-1}). Samples (3×3 cm^2), dried at 40°C in vacuum, were sandwiched between the reflection crystal (KRS-5) and the back plate. Spectra were taken with air as the background. The resolution and the number of scans were 4.0 cm^{-1} and 32, respectively. The amount of grafted PAA was determined by a titration method. The grafted membrane was placed in 0.01*N* NaOH, shaken for 24 h, and then the solution was titrated against 0.001*N* HCl solution.

TABLE I
PAA/PVDF Composite Membranes for Pervaporation

Sample code	Amount of grafted PAA (mg/cm^2)	Number of PAA layers
S-4	0.40	1
S-6	0.58	1
S-8	0.84	1
S-10	0.95	1
D-6	1.08	2
D-8	1.66	2
D-10	1.89	2
T-8	Two D-8 membranes	3

In this research, composite membranes with PAA/PVDF/PAA sandwich-type of structure (hereafter called 2PAA-layer membrane) and PAA/PVDF/PAA/PVDF/PAA multilayer structure (hereafter called 3PAA-layer membrane) were also fabricated. The former was prepared by treating both top and bottom surfaces of the PVDF membrane with plasma and then grafting them with PAA. To prepare the 3PAA-layer membrane, two 2PAA-layer membranes were fused together by first wetting two PAA surfaces with water and then lightly pressing the membranes together. Finally, the composite membrane was allowed to dry at 60°C in vacuum. Table I summarizes the prepared composite membranes with different multilayer structure and grafting amounts of PAA. These membranes were used in subsequent pervaporation processes.

Pervaporation

Pervaporation experiments of various membranes were carried out on ethanol/water solutions at room temperature following a procedure described in the literature. The feed was maintained at approximately constant composition during each experiment by regularly measuring the feed concentration and adding fresh solutions into the feed tank. The permeate was collected by a liquid nitrogen cold trap and its ethanol content was analyzed using gas chromatography.

RESULTS AND DISCUSSION

Formation of PAA/PVDF composite membranes

PVDF membranes, used as substrates for preparing PAA/PVDF composite membranes, were characterized by a microporous structure, as shown in Figure 1. The top surface of the membrane is composed of large clusters of PVDF crystallites in a more or less spherical shape [Fig. 1(a)]. The boundaries between those crystallites often break into large crevices (~ 1 μm), some

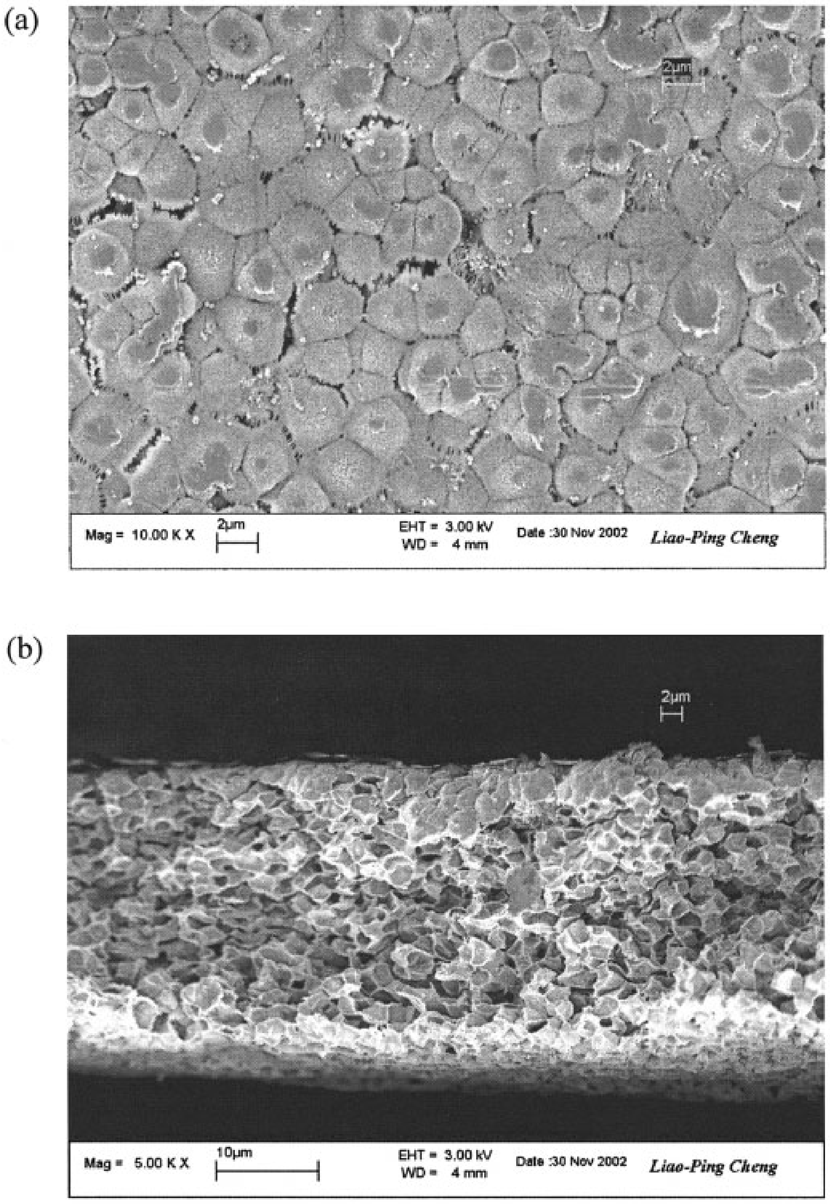

Figure 1 SEM photomicrographs of a PVDF membrane with a skinless structure: (a) top surface; (b) cross section.

of which appear to interconnect with the pores in the cross section. The structure of the cross section is shown in Figure 1(b). It is porous and all of the pores are open and interconnected to form numerous channels within the polymer matrix. This membrane also possesses reasonably satisfactory mechanical strength. It is thus considered as a good supporting material for preparing composite membranes with PAA for the purpose of pervaporation.

PAA was grafted by plasma-induced polymerization on the surface of a PVDF substrate. The presence of PAA on the PVDF membrane was verified by FTIR/ATR analysis. Figure 2 shows the spectrum of a typical PAA/PVDF composite membrane together with that of a pure PVDF substrate. The absorption peak at 1710 cm^{-1}, characteristic of the C═O of PAA, is evident for the composite membrane, yet it is not observed for the pure PVDF substrate. The grafting yield for common plasma-induced free-radical polymerization, as discussed in the literature, depends on factors such as plasma treatment time, concentrations of reactants, reaction temperature, reaction time, and so forth.[18–25] In the present research, attention has been focused on the effects of the monomer concentration and the reaction time. Figure 3 demonstrates the amounts of grafted PAA as a function of reaction time and monomer concentration. It can be seen that the grafting yields increase monotonously with increasing reaction time for all monomer concentrations (10–80% AA). Given the fact that only a definite quan-

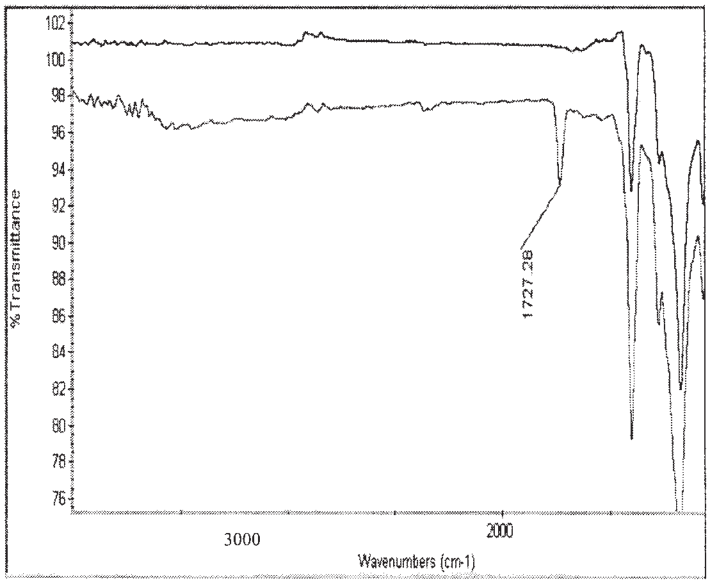

Figure 2 FTIR spectra of PVDF and PAA/PVDF composite membranes: (a) pure PVDF; (b) grafting yield = 0.95 mg/cm^2.

tity of active sites were generated on the surface of PVDF by plasma bombardment, the increase of PAA was attributed to growth of the PAA chain rather than creation of new polymer chains. Because the bulk solution also underwent free-radical polymerization at an elevated temperature (80°C), the reaction mixture gelled or solidified after a certain period of time, depending on the initial concentration of AA. For an already gelled sample, characterization of the PAA/PVDF composite membrane was difficult, and the data are not reported here. Figure 3 also shows the effects of initial AA concentration. At first, the grafting yield increases with increasing AA over the range 10–50 wt %; however, as the concentration exceeds 50 wt %, the grafting yield begins to decrease. In our opinion, there are two possible reasons for this uncommon phenomenon: (1) for very high AA concentration cases, growth of grafted PAA chains could be retarded or even terminated by an early gelation of PAA in the bulk. For example, a bulk solution of 80 wt % AA gelled about 5 h earlier than that of 50 wt % AA. (2) At high AA concentrations, the PVDF surface was likely to form a PAA layer rapidly, which might serve as a resistive layer that impeded monomers to diffuse through it. Thus, within the PAA layer there might contain shorter grafted chains. However, the real causes of this experimental result are subject to further investigation.

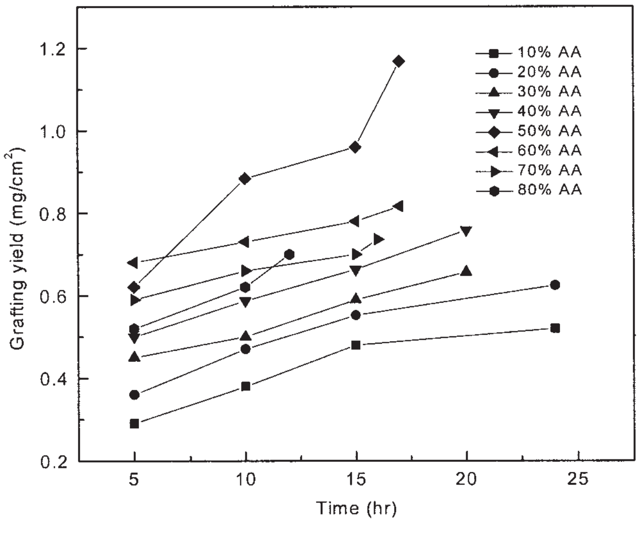

Figure 3 Effect of acrylic acid concentration and reaction time on the grafting yield of PAA.

Figure 4 shows the SEM image of the grafted (top) surface of two typical composite membranes. For the case of low grafting yield, as in Figure 4(a), the top surface still has defected sites (pores), whereas in the case of high grafting yield, the substrate is covered with a thick and dense layer of PAA, which functions as an effective permselective layer in pervaporation operations. 2PAA and multi-PAA layer membranes were prepared by the procedures described earlier in the experimental section. The grafting yields are summarized in Table I. The sample codes S-, D-, and T- depict membranes containing one, two, and three PAA layers, respectively. For example, membrane D-8 was assembled by fusing together two S-8 membranes, whereas T-8 was assembled by fusing of two D-8 membranes. In Figure 5, the cross-sectional structure of a 3PAA-layer membrane is demonstrated. There one may observe a very thin PAA layer in the middle between the two porous PVDF supports. Because there is only physical bonding (e.g., entangle-

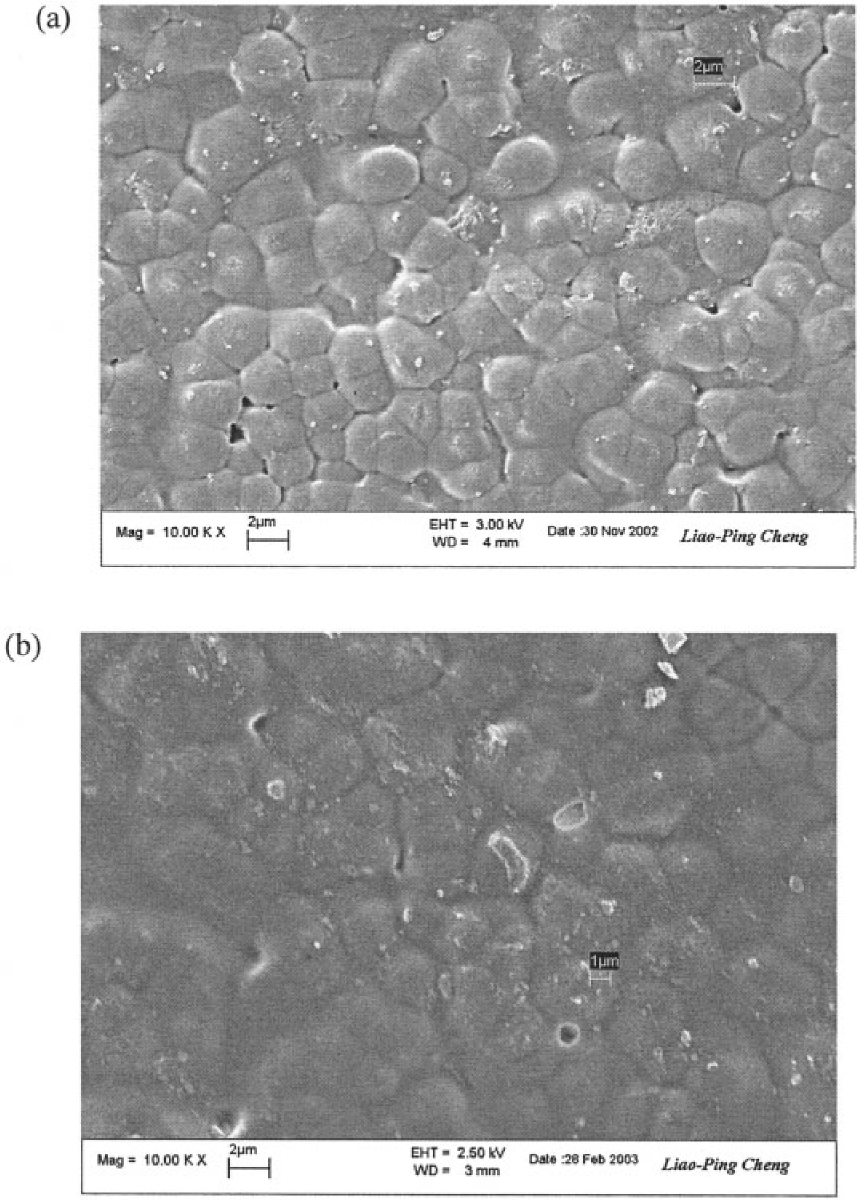

Figure 4 SEM photomicrographs showing the grafted surface of the PAA/PVDF composite membranes: (a) grafting yield = 0.4 mg/cm^2; (b) grafting yield = 0.85 mg/cm^2.

ment) between the two joining PAA layers, they will break apart upon soaking in water for an extended period of time. Hence, such multilayer arrangement can be used only in specific separation operations, such as pervaporation, which is further discussed later. It is also possible to prepare a multilayer composite membrane with the intermediate PAA layer of approximately the same thickness as that of the top or bottom PAA layer by combining 2PAA-layer membranes whose top and bottom surfaces have different amounts of PAA. In this case, a nonuniform PVDF substrate, with very different top and bottom surface porosity, has to be used. This appears to be an interesting work for future investigation.

Pervaporation

Pervaporation of ethanol/water solutions were carried out using membranes with different graft yields and multilayer configurations. In Figure 6, the separation factors and the permeation fluxes are shown for the cases of 1PAA-layer membranes with different amounts of grafted PAA. It appears that at low grafting yield (e.g., 0.4 mg/cm^2) the separation was poor because of the fact that the PVDF substrate was not fully covered with grafted PAA [cf. Fig. 4(a)], and thus both ethanol and water could pass easily through the large pores of the membrane. As the grafting yield was increased, the separation factor also increased,

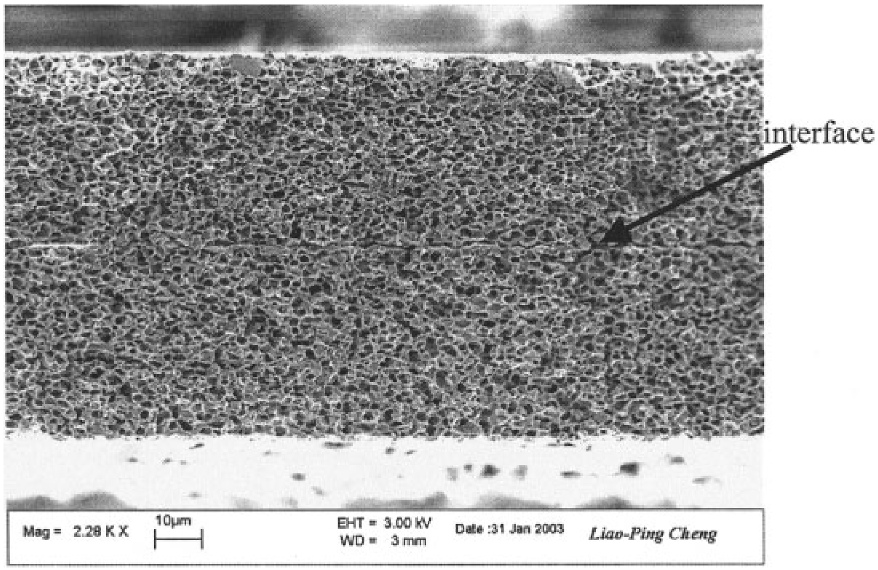

Figure 5 SEM photomicrographs showing the cross sections of a composite membrane with three separate PAA layers (top, intermediate, bottom).

although at the sacrifice of permeation fluxes as in normal pervaporation processes. When the grafting yield reached about 0.84 m g/cm^2, there was a significant improvement of the separation factor over the entire concentration range, suggesting that the PAA had already formed an effective resisting layer on the porous top surface of the PVDF substrate [cf. Fig. 4(b)]. For grafting yield higher than 0.84 mg/cm^2, the increment leveled off, increasing only slightly with increasing amount of PAA. Similar results were also reported in the literature for different systems.[12,23,24,26] In particular, Yamaguchi et al.[12] prepared composite membranes by plasma-grafted filling polymerization. As the amount of grafting reached the point where pores were completely filled with grafted polymers, the separation factor no longer increased with increasing grafting yield. Figure 6(a) also indicates that the separation factor increases with increasing feed ethanol contents, just the same as for common water-selective membranes. For this type of membranes, the degree of swelling of the permselective layer was lower for feed with higher ethanol concentration. This results in a smaller permeation flux and higher separation factor in the high ethanol concentration region.[13,14,23–25,27] However, there are exceptions; for example, there may exist a maximum separation factor in the intermediate concentration range.[4,14,18]

For a very high grafting yield of 0.95 mg/cm^2 in the present research, the separation factor is only 4.26 for the 50 wt % ethanol feed, which is still too low for practical purposes. To increase the separation factor, membranes with a multilayer configuration were developed. Tables II–IV summarize the pervaporation performances of such kinds of membranes. For illus-

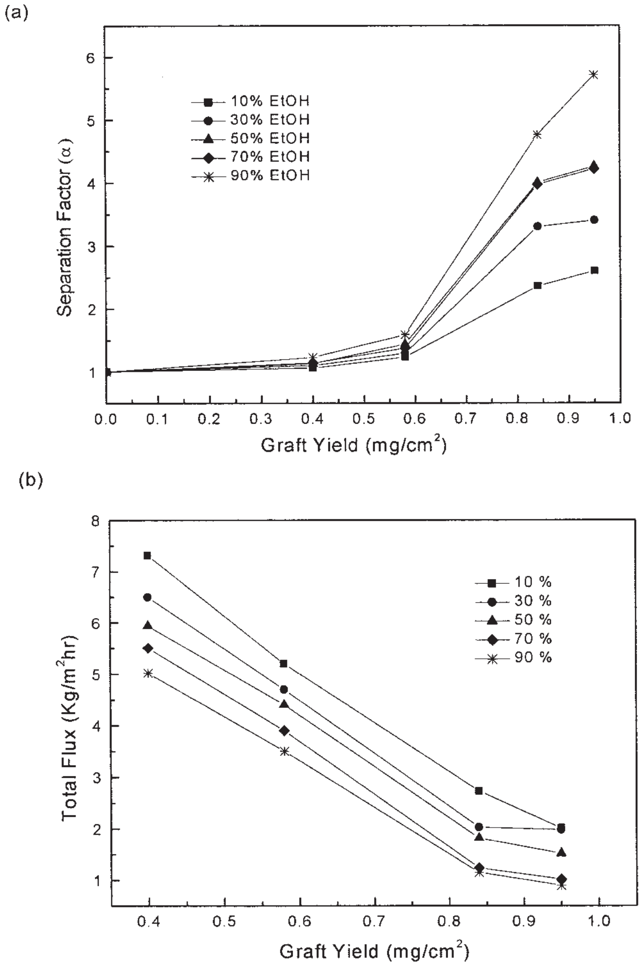

Figure 6 Effect of grafting yields on the separation factors and permeation fluxes of four 1PAA-layer composite membranes (S-4, -6, -8, -10): (a) separation factor; (b) permeation flux.

TABLE II
Pervaporation Performances of Composite Membranes S-6 and D-6

Sample code	Feed ethanol (%)	Permeate ethanol (%)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	PSI
S-6	10	8.3	5.2	1.23	6396
	30	25	4.7	1.29	6063
	50	41	4.4	1.44	6336
	70	63	3.9	1.37	5343
	90	85	3.5	1.59	5565
D-6	10	3.5	2.50	3.06	7650
	30	11.5	2.31	3.3	7623
	50	22	2.02	3.55	7171
	70	39	1.97	3.65	7191
	90	69.2	1.95	4.01	7820

tration, some representative results for the 2PAA- and 3PAA-layer membranes are shown in Figure 7, together with that having only one PAA layer (grafting yield = 0.85 mg/cm^2). It can be seen that the separation factors increase on the order of 10 times from single to double PAA-layer membranes. Such dramatic improvement can be attributed to the special separation mechanism associated with the 2PAA-layer membrane. For this membrane, the outer PAA layer functions like the permselective layer of a normal

TABLE III
Pervaporation Performances of Composite Membranes S-8, D-8, and T-8

Sample code	Feed ethanol (%)	Permeate ethanol (%)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	PSI
S-8	10	4.5	2.73	2.36	6443
	30	11.5	2.03	3.3	6699
	50	20	1.82	4.0	7280
	70	37	1.15	3.97	4566
	90	65.4	1.24	4.76	5902
D-8	10	0.15	0.32	74	23680
	30	0.73	0.31	58.3	18073
	50	2.5	0.30	39	11700
	70	6.6	0.32	33	10560
	90	20.6	0.30	34.7	10410
	95	34.5	0.28	36.1	10108
T-8	50	0.9	0.09	110.1	9909
	70	2.1	0.09	108.8	9683
	90	7.6	0.09	109.4	9955
	95	15	0.09	107.7	9908

TABLE IV
Pervaporation Performances of Composite Membranes S-10 and D-10

Sample code	Feed ethanol (%)	Permeate ethanol (%)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	PSI
S-10	10	4.1	2.01	2.6	5,225
	30	11.2	1.98	3.4	6,732
	50	19	1.52	4.26	6,475
	70	35.6	1.02	4.22	4,304
	90	61.2	0.90	5.71	5,139
D-10	50	1	0.24	99	23,760
	70	3	0.24	75.44	18,106
	90	12	0.24	66	15,840
	95	25	0.24	57	13,680

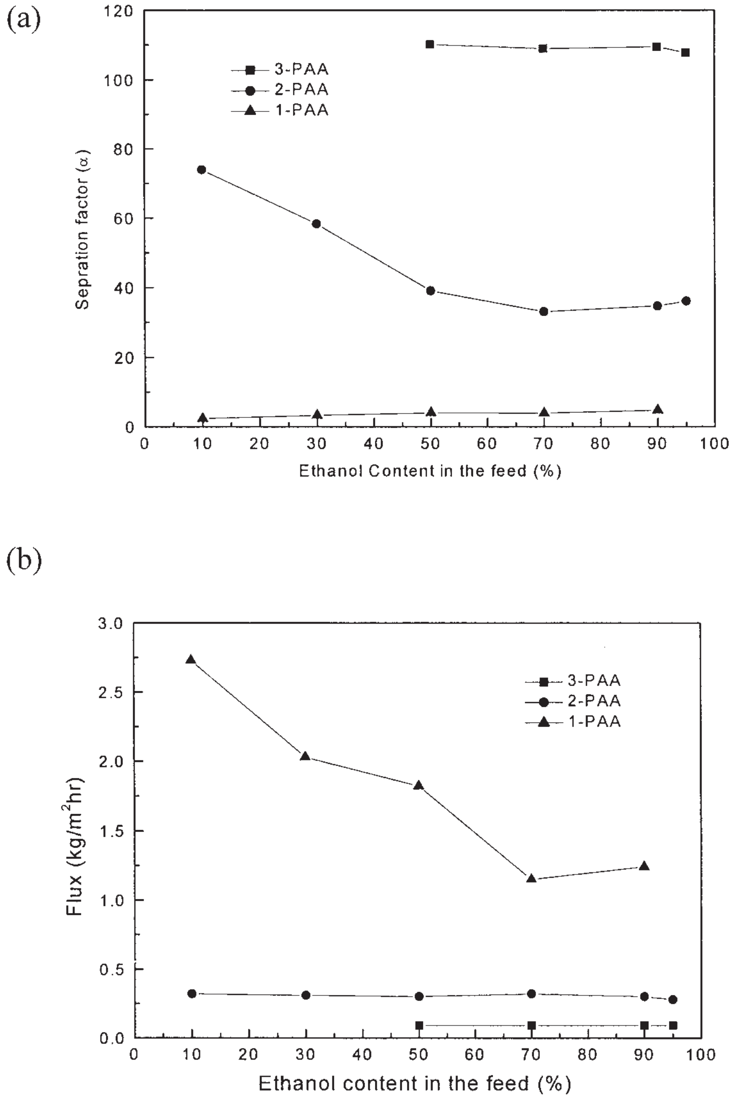

Figure 7 Pervaporation performance of multilayer composite membranes S-8, D-8, and T-8: (a) separation factor; (b) permeation flux.

pervaporation membrane, which contacts the liquid feed solution directly. In contrast, the second PAA layer contacts a gaseous permeate from the outer layer; therefore the separation is governed by a process similar to gas separation. For the outer PAA layer, it is expected that swelling by water and ethanol is significant near the interfacial region. Therefore, separation of these two species depends on their mutual interactions (i.e., the cross-term has to be considered), in addition to their individual capabilities to dissolve in and diffuse through the PAA layer. However, for the second PAA layer, swelling is minimal because of the very low permeate density (cf. permeation flux data in Table II). Thus, water and ethanol are essentially noninteractive as they go through this PAA layer. In this case, separation of these two species becomes relatively effective because water can dissolve and diffuse through the membrane without being affected by the sluggish ethanol.

A well-known operation, somewhat similar to that for the second PAA layer, is the vapomeation process.[15,16,27–29] In this process, liquid feed solution is evaporated before passing through a membrane that is mounted above the feed. Therefore, the excessive swelling that may cause poor separation or even membrane failure can be avoided. It was generally found that the separation factor is higher and the permeation flux is lower for vapomeation than for pervaporation using the same membrane. Figure 7(a) also indicates that the separation factor for the 2PAA-layer membrane is highest for feeds in the low ethanol concentration region (e.g., $\alpha = 74$ for 10% ethanol feed). This trend is opposite to that for the 1PAA-layer membrane, in which swelling is more significant at lower ethanol concentrations. Given that swelling is insignificant for the second PAA layer, the gaseous permeate from the first layer with less ethanol content is thought to be more favorable for water permeation. However, solid evidences have not yet been found to confirm this argument.

The permeation flux of the 2PAA-layer membrane is shown in Figure 7(b). Quite interestingly, the total fluxes stay nearly constant over the tested concentration range, with only a slight decrease at the very high concentration end. The fluxes of the 2PAA-layer membrane can be compared with that of the 1PAA-layer membrane (cf. also Table III). It appears that the 2PAA-layer membrane has lower fluxes and higher separation factors. Moreover, the extent of decrease in flux (with respect to 1PAA-layer membrane) was less than the extent of increase in the separation factor. As a result, the PSI of the 2PAA-layer membrane is 2–4 times higher than that of the 1PAA-layer membrane, depending on the concentration of the feed. To further increase the separation capability, a membrane with three separate PAA layers was prepared. Its pervaporation performance is also shown in Figure 7. For all tested feed concentrations, the separation factors are higher than 100 and the permeation fluxes are close to 0.1 kg m^{-2} h^{-1}. The PSI values are close to those of the 2PAA-layer membranes operating at the same feed concentrations. Because the permeation of the 3PAA-layer membrane involves one additional gas separation, it is expected to exhibit a higher separation factor and a lower flux than the 2PAA-layer membrane. Hence, if products of high purity are desirable, multiple-layer membranes offer a good choice.

CONCLUSIONS

Novel multilayer composite membranes were prepared and used in a pervaporation process to separate ethanol/water solutions. These membranes had their permselective layers and porous mechanical supports arranged in a PAA/PVDF/PAA/··· alternating configuration. As a result of integrating gas separation into a traditional pervaporation process, these membranes demonstrated superb pervaporation performance compared with that of traditional membranes that had only one active permselective layer.

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