Modified Silicone–PVDF Composite Hollow-Fiber Membrane Preparation and Its Application in VOC Separation

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ABSTRACT: Polydimethylsiloxane^{vi}–poly(vinylidene fluoride) (PDMS^{vi}–PVDF) composite membranes were prepared using asymmetric PVDF hollow-fiber membranes as the substrate where a very thin layer of silicone-based coating material was deposited via a developed dip coating method. The preparation of the composite membranes under various conditions were investigated. In the optimal coating procedure, homogenous and stable oligo-PDMS^{vi} coating layers as thin as 1–2 μm were successfully deposited on the surface of PVDF membranes. The developed PDMS^{vi}–PVDF composite membranes were applied for separation of a wide variety of volatile organic compounds (benzene, chloroform, acetone, ethyl acetate, and toluene). The results showed that the PDMS^{vi}–PVDF hollow-fiber composite membranes that had been developed exhibited very high removal efficiency (>96%) for all the VOCs examined under favorable operating conditions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2497–2503, 2006

Key words: poly(vinylidene fluoride) (PVDF); composite; membrane

INTRODUCTION

Separation of volatile organic compounds (VOCs) by vapor permeation is based on the use of a thin-film composite membrane that is highly permeable to organics but is relatively impermeable to air and other permanent gases.[1,2] Despite its relatively short industrial history of development, vapor permeation is well recognized from an economic point of view, especially when valuable organic vapors such as reusable solvents and aroma and flavor essences are involved.[3] To date, recovery of halogenated hydrocarbons, gasoline vapors, and organic solvents from air remains a major industrial problem.

To remove higher-molecular-weight organic vapors from air, ideal membranes must be extremely permeable to organic vapors and relatively impermeable to air or nitrogen. Conventional polymeric membranes such as cellulose acetate and polysulfone are not suitable for VOC separation from air or nitrogen because they are made from glassy polymers and generally favor smaller and lighter molecules, which diffuse faster. In contrast, rubbery polymers are more permeable to bigger and heavier VOC molecules than to light gases. Most of the pioneer work in this area has focused on silicone-rubber-coated composite membranes using polydimethylsiloxane (PDMS).[4–8] The composite membranes used in vapor permeation also require the support membranes to be highly permeable and solvent resistant. In this context, poly(vinylidene fluoride) (PVDF) appears to be an ideal material because of its excellent chemical stability and ease of processing into support membranes with high gas permeability. Although other support membranes such as polysulfone and poly(ether sulfone) also have shown high permeation characteristics, they are not suitable for use in vapor permeation because they are easily attacked in many solvents.

Over the past few years, an oligosilylstyrene, a vinyl-terminated PDMS crosslinking material, was prepared, and the PDMS^{vi} crosslinked by this oligomer, oligo-PDMS^{vi}, has been found capable of efficiently separating chlorinated and aromatic hydrocarbons from liquid water by pervaporation[9] as well as aromatic hydrocarbons from nitrogen by vapor permeation.[10] In this study, PDMS^{vi}–PVDF composite hollow-fiber membranes were prepared based on a four-step coating procedure that had been developed, which consists of: (1) fast dip coating, (2) precrosslinking, (3) vacuum coating, and (4) final crosslinking. Coating thickness, uniformity, and integrity were examined through gas permeation and SEM.

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TABLE I
Characteristics of the PDMS^{vi}–PVDF Composite Membrane Modules Used for Vapor Permeation

	PVDF	VF	ID/OD of module (cm)	OD of HF (cm)	No. of fibers	EFL (cm)	MA (cm^2)	CLT (μm)
Module 1	PVDF(2)	0.63	0.620/0.958	0.077	24	38	220.6	4~5
Module 2	PVDF(2)	0.85	1.068/1.276	0.077	29	39	271.8	2.5
Module 3	PVDF(1)	0.60	0.620/0.958	0.072	19	40	171.9	1.0

ID: inner diameter; OD: outside diameter; VF: hollow-fiber volume fraction; HF: hollow fibers; EFL: effective fiber length; MA: effective separation area; CLT: coating layer thickness.

The parameters affecting the integrity and performance of the composite membrane prepared by the coating method were investigated. The composite membranes prepared under optimum coating conditions were applied to the separation of a wide variety of VOCs from N_2.

EXPERIMENTAL

Preparation of composite membranes

Poly(vinylidene fluoride) (PVDF) asymmetric hollow-fiber membranes were prepared from polymer dopes formulated from PVDF as the polymer, *N,N*-dimethylacetamid (DMAc) as a solvent, and lithium chloride as a nonsolvent additive. The PVDF (Kynar® K760) was supplied by Elf Atochem (USA), whereas the solvent and additive were purchased from Merck. The chemicals used were all analytical grade and were used without further purification. The membranes were spun via a dry–wet phase inversion method with tap water as both the internal and external coagulants. Details of the spinning process were presented previously.[11] PVDF hollow fibers of varying porosity were spun using different polymer dopes under different spinning conditions.[11]

Coating solutions consisted of oligosilylstyrene as a crosslinker, divinyl-terminated polydimethylsiloxane (PDMS^{vi}; 1000cs; United Chemicals Technologies, Inc.; analytical grade), and platinum-divinyltetra-methyldisiloxane complex as a Karstedt's catalyst (United Chemicals Technologies, Inc.; analytical grade). Each of the three components was prepared using hexane (analytical grade, J.T. Baker) as the solvent and then all solutions were mixed together. The solution was well mixed in a shaker for hours before the coating process.

Formulation of ultrathin composite membranes by the solution coating method consists of four main steps: (1) fast dip coating, (2) pre-crosslinking, (3) vacuum coating, and (4) final crosslinking. The coated hollow-fiber membranes were then made into prototype modules, and tests of possible surface defects of the composite membrane were carried out using standard nitrogen and oxygen permeation experiments.

Three modules were fabricated using the composite hollow fibers prepared for future VOC separation. The characteristics of the modules are listed in Table I.

Characterization of composite membranes

A gas permeation method was employed to test for possible surface defects in the composite hollow-fiber membranes using nitrogen and oxygen (99.99% purity, BOC), which were fed individually into the shell side of the membrane over a pressure range of 1.0–3.0 KPa. The permeation values of each gas were calculated from the permeation obtained using a soap bubble meter, and thus, oxygen/nitrogen (O_2/N_2) selectivity values were obtained in order to determine whether the composite membranes were defect free.

The integrity as well as the uniformity of the composite membranes was confirmed using a scanning electron microscope (JEOL-5600LV).

Vapor permeation

The experimental setup for VOC/N_2 separation is shown schematically in Figure 1. A nitrogen stream from a cylinder was introduced into a stainless-steel bubbler filled with VOC. This stream was then mixed with a second stream of pure N_2 to produce a stream of the desired VOC concentration and flow rate. Vacuum was applied countercurrently on the lumen side of the module. A cold trap was connected between the vacuum pump and the hollow-fiber module to recover the VOC from the gas streams. A Perkin Elmer 8700 gas chromatograph was used to analyze the concentrations of samples taken from the feed, permeate, and residue streams using a FID detector.

RESULTS AND DISCUSSION

Characterization of PDMS^{vi}–PVDF composite membranes

Cross-sectional structures of the PVDF support membranes and its coated composite membranes are shown in Figure 2. It can be seen from Figure 2(a) that

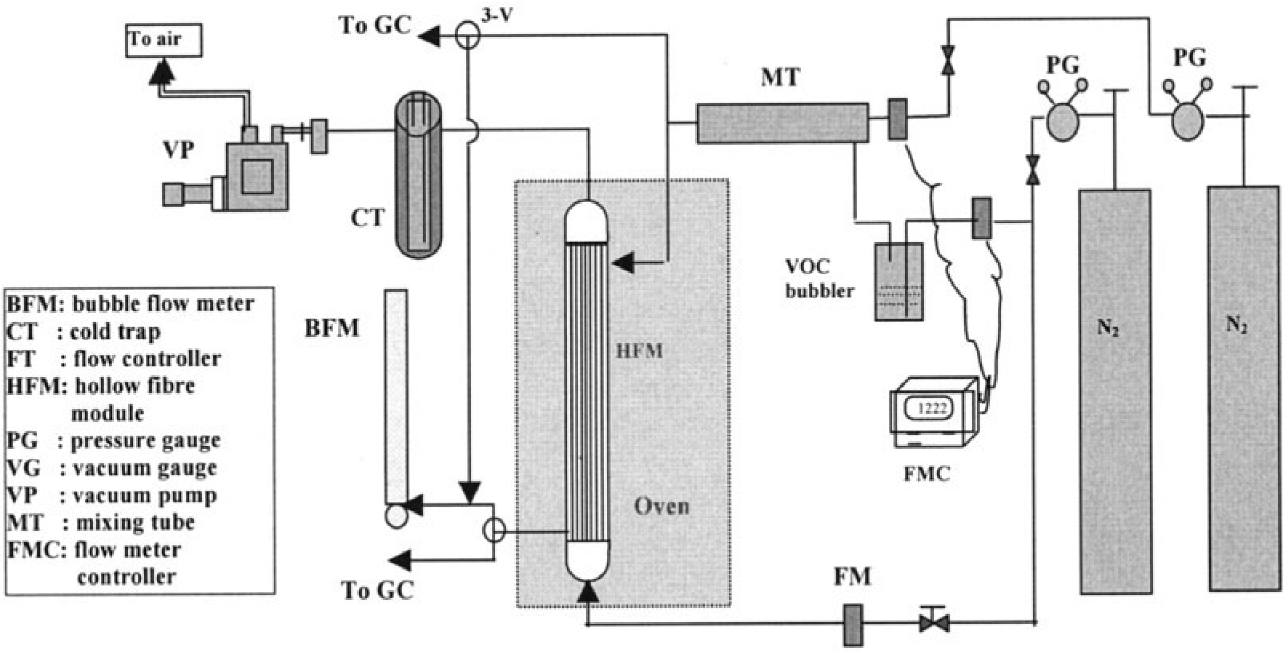

Figure 1 Experimental setup for VOC/N_2 separation by vapor permeation.

an integrated asymmetric PVDF hollow-fiber support membrane was obtained via the dry/wet spinning process.[11] The inner layer of the support membrane was designed to be much more porous than the outer layer. Also, support membranes with two different surface roughness of the outer layer were prepared and employed in the coating process. Using the dip coating technique described above, the PDMS^{vi}–PVDF composite hollow-fiber membranes were prepared. As shown in Figure 2(b,c), an ultrathin dense oligo-PDMS^{vi} layer was deposited on the PVDF substrate. The coating was stable and fairly uniform, with a thickness at about 1–2 μm for PVDF(1) [Fig. 2(b)] and 2–3 μm for PVDF(2) [Fig. 2(c)]. The coating layer exhibited a smooth, relatively uniform surface, and SEM examination of the composite membranes fabricated revealed that an ultrathin, dense, and homogenous oligo-PDMS^{vi} coating layer could be successfully deposited on the asymmetric PVDF hollow-fiber membrane using the described four-step coating procedure.

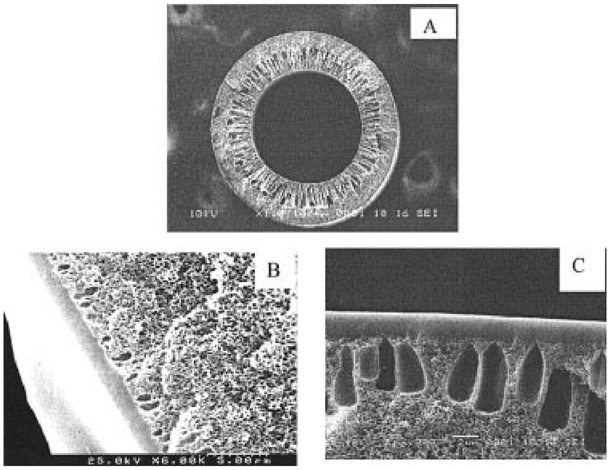

Figure 2 Cross-sectional structures of PVDF hollow fiber and its composite membranes (fast dip coating time = 30 s; vacuum coating time = 2 min, P_d = 2 cmHg): (a) PVDF(1) support membrane, (b) PDMS^{vi}–PVDF(1) composite membrane, (c) PDMS^{vi}–PVDF(2) composite membrane.

A comparison of SEM pictures shown in Figure 2(b,c) reveals that the coating thickness may be related to the surface roughness of the support membranes. Both composite membranes—PDMS^{vi}–PVDF(1) and PDMS^{vi}–PVDF(2)—were fabricated under the same coating condition. The only difference was that the support layer of PVDF(2) had a much rougher outer surface than that of PVDF(1). As a result, the thickness of the coating layer of PDMS^{vi}–PVDF(2) was almost double that of PDMS^{vi}–PVDF(1), as shown in Figure 2(b,c). It follows that the rougher surface of the PVDF(2) support membrane was easier to coat, resulting in a thicker coating layer in the same coating conditions.

The composite membranes prepared by dip coating without applied vacuum displayed very poor integrity, as shown in Figure 3. As can be seen, there appeared to be a gap between the oligo-PDMS^{vi}-coated layer and the PVDF substrate. As a result, the coated layer was unstable and was delaminated easily from the substrate when an elevated pressure was applied in the lumen of the hollow fiber. This indicates

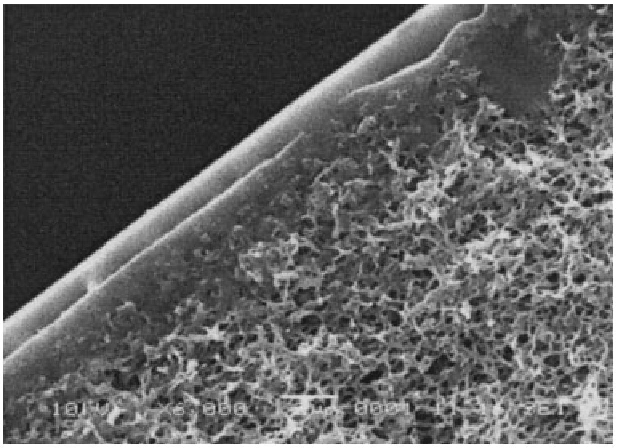

Figure 3 Cross-sectional structure of the composite membrane without vacuum coating [solution mixing time = 24 h; PVDF(1) support; fast dip coating time = 30 s, final coating time (at 1 atm) = 2 min; pre-crosslinking time = 24 h; final crosslinking temperature = 24°C].

that the bonding between the coated layer and the porous substrate was weak for dip coating under atmospheric pressure. When the pressure in the fiber lumen was reduced, the driving force created strengthened the adherence of the coating layer to the PVDF substrate. Both the degree of applied vacuum and the duration were critical in achieving the desire coating layer thickness and its integrity.

Figure 4 illustrates the effect of vacuum coating on the permselectivity of the prepared PDMS^{vi}–PVDF membrane. It can be seen from Figure 4(a) that for PDMS^{vi}–PVDF(1), the effect of vacuum level on N_2 permeation was only marginal, whereas the O_2/N_2 selectivity increased from 2.0 to 2.5 when the coating pressure was reduced from 45.8 to 4 cmHg. The result suggests that a greater vacuum (lower operating pressure) during the coating process is favorable for preparing defect-free composite membranes. This is because the high vacuum increased the homogeneity of the coating layer with negligible effect on its thickness.

As for the PDMS^{vi}–PVDF(2) composite membrane, the results presented in Figure 4(b) show that O_2/N_2 selectivity remained fairly constant over the entire range of vacuum levels applied. However, N_2 permeation was favored at a low vacuum level (i.e., a higher operating pressure). The latter observation suggests that the coating layer thickness increased, as the vacuum level was increased, resulting in higher membrane resistance and hence lower N_2 permeation.

The effect of duration of vacuum coating also was studied using the PVDF(1) support membrane. The results tabulated in Table II reveal that the three PDMS^{vi}–PVDF(1) composite membranes, prepared with different vacuum coating times, displayed good integrity and comparable permselectivity. A closer comparison of these results suggests that a longer coating time yielded higher selectivity. Thus, a vacuum coating time of 2–4 min was chosen for subsequent experimental work.

In addition to the effects of the surface roughness of PVDF, vacuum coating level, and vacuum coating time on coating thickness, uniformity, and integrity, other operating factors that may have influenced the coating results also were studied. These factors include PDMS^{vi} concentration in the solution, coating solution mixing time, crosslinking temperature, and duration of crosslinking. The observed optimal conditions of these parameters are summarized in Table III.

VOC/N_2 separation

The removal of a wide variety of volatile organic compounds (VOCs) by vapor permeation from VOC/N_2 mixtures was investigated using the developed PDMS^{vi}–PVDF composite membranes. The VOCs tested in this study included benzene, toluene,

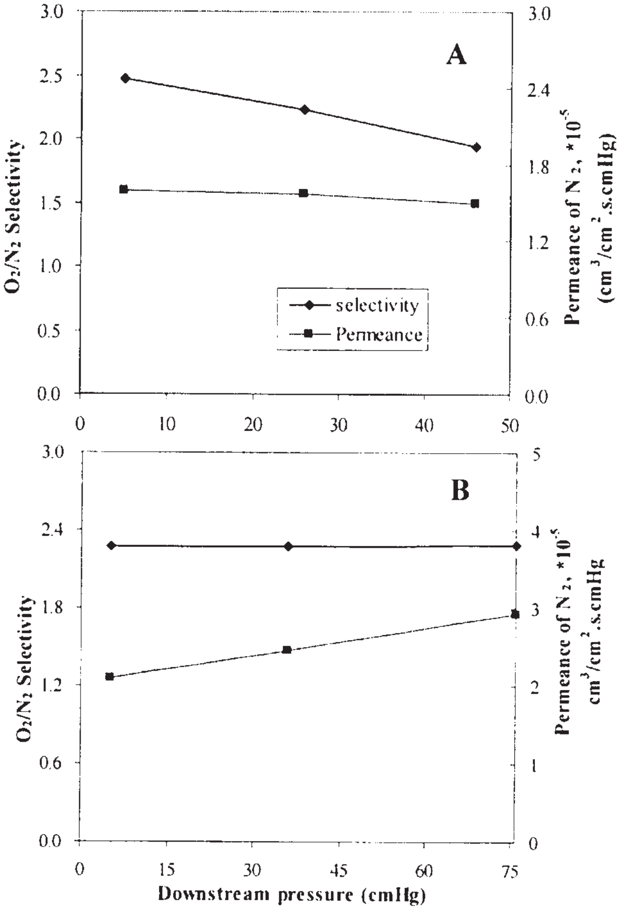

Figure 4 Effect of vacuum level on permselectivity of: (a) PDMS^{vi}–PVDF(1) and (b) PDMS^{vi}–PVDF(2) composite membrane (solution mixing time = 24 h; fast dip coating time = 30 s; vacuum coating time = 2 min; final crosslinking time = 24 h).

TABLE II
Effect of Vacuum Coating Time on Preparation of Composite Membranes [$PDMS^{vi}$– PVDF(1); P_d = 2 cmHg]

	Solution conc. (wt %)	Solution mixing time (h)	Fast dip coating time (s)	Vacuum coating time (min)	Crosslinking time (h)	O_2/N_2 selectivity	N_2 permeation [cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$]
1	10	24	30	2	24	2.34	1.43×10^{-5}
2	10	24	30	1	24	2.17	1.44×10^{-5}
3	8	24	30	4	24	2.28	1.59×10^{-5}

chloroform, ethyl acetate, acetone, and pentanone, which are commonly found in various industries.

The effect of feed concentration and feed flow rate on the benzene flux and removal efficiency in module 1 (Table I) is shown in Figure 5. As depicted, the benzene flux exhibited a fairly good linear relationship with the benzene feed concentration. The results revealed that increases both in the feed concentration and the flow rate would enhance the mass transfer of benzene across the composite membrane, in general agreement with the solution–diffusion model.

Effects of benzene feed concentration and feed flow rate on removal efficiency are illustrated in Figure 6. The results indicated that very high removal efficiency, from 96% to 99.9%, was achieved for all the experimental conditions tested. The highest removal efficiency, 99.9%, was achieved at the lowest flow rate of 200 mL/min over the entire feed concentration range examined. At higher flow rates, of 300 and 400 mL/min, removal efficiency was lower. However, it was still as high as 99% and 96%, respectively. The higher removal efficiency attained at lower feed flow rates was of course a result of the longer contact time between the VOC vapor and the membrane surface. The results shown in Figure 6 also illustrate that removal efficiency at these flow rates was independent of feed concentration over the concentration range studied.

TABLE III
Optimum Coating Conditions for Preparation of $PDMS^{vi}$–PVDF Composite Membrane

Coating-influencing factor	Optimum condition
Coating solution concentration (wt %)	10
Solution mixing time (h)	~24
Fast dip coating time (s)	30–45
Vacuum coating time (min)	2–4
Support membrane	Substrate with moderate porosity
Downstream pressure, P_d (cmHg)	2–10
Pre-crosslinking time (h)	2–4
Final crosslinking time (h)	12–24
Crosslinking temperature (°C)	24–50

Separation of the chloroform/N_2 system using a $PDMS^{vi}$–PVDF composite membrane (module 1) also was investigated at different operating conditions. Figure 7 illustrates the effects of feed flow rate and feed concentration on the removal efficiency of the chloroform/N_2 system. As shown, chloroform removal efficiency was generally very high, especially at the low flow rate of 300 mL/min. It decreased slightly with feed concentration over the examined range of 15,000–175,000 ppmv. On the other hand, the results showed a significant effect of feed flow rate on chloroform removal efficiency, which decreased as the feed rate increased. The removal efficiency dropped noticeably from 96% to 89% when the feed flow rate was increased from 300 to 500 mL/min. The reduction in efficiency with flow rate was similar to that of the benzene/N_2 system and can be attributed to the reduced VOC-membrane contact time, as discussed before.

The results of the composite membrane used for acetone/N_2 separation for both tube-side and shell-side feed operations are shown in Figure 8. As illus-

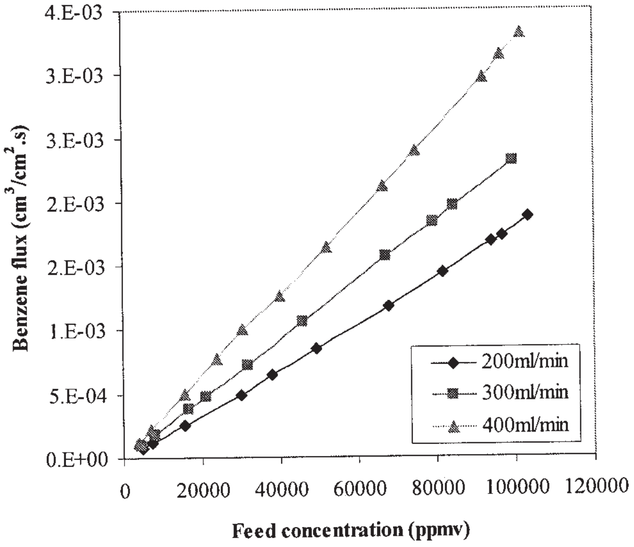

Figure 5 Variation of benzene flux with benzene feed concentration at different feed flow rates [module 1, shell-side feed; operating conditions: T = 50°C, feed pressure (P_f) = 1 bar, downstream pressure (P_d) = 8 mbar].

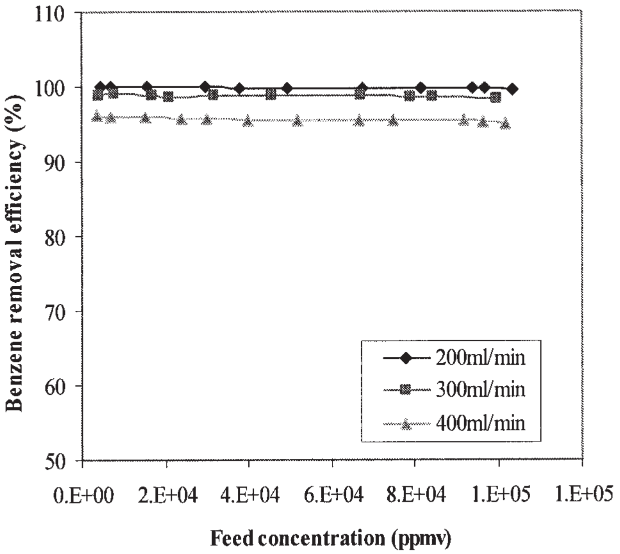

Figure 6 Variation of benzene removal efficiency with benzene feed concentration at different feed flow rates (module 1, shell-side feed; operating conditions: $T = 50°C$, $P_f = 1$ bar; $P_d = 8$ mbar).

trated, acetone removal efficiency was in the range of 95%–99% in the tube-side feed operation and 82%–92% in the shell-side feed operation. Acetone removal efficiency was significantly higher in the tube-side feed operation over the flow rate range studied. These observations generally agreed well with the reported results.[12] As anticipated, better and more efficient VOC and membrane surface contact would be achieved in tube-side feed because of more uniform vapor distribution. Also, the tube-side feed operation had fewer problems of channeling and bypassing as those in shell-side feed. The separation of other VOC/N_2 systems such as toluene, ethyl acetate, and pentanone in the PDMS^{vi}–PVDF composite membrane modules also was carried out, and the results are summarized in Table IV.

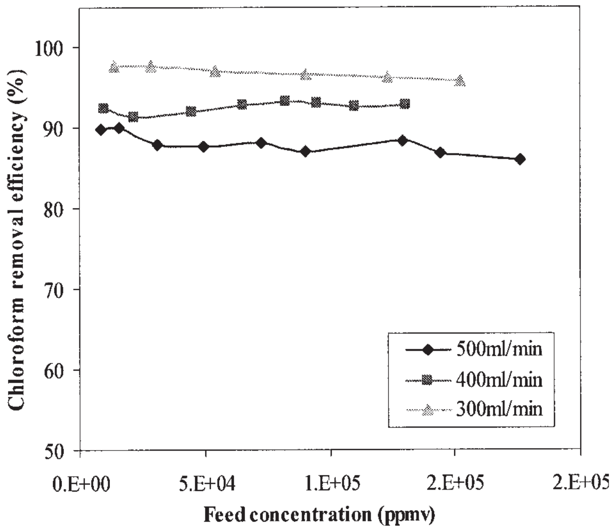

Figure 7 Variation of chloroform removal efficiency with chloroform feed concentration at different feed flow rates (module 1, shell-side feed; operating conditions: $T = 50°C$, $P_f = 1$ bar; $P_d = 8$ mbar).

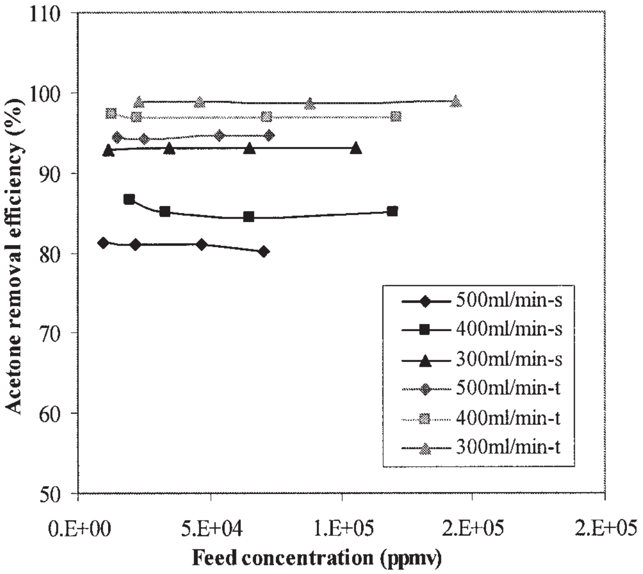

Figure 8 Variation of acetone removal efficiency with acetone feed concentration at different feed flow rates (module 1 operating conditions: $T = 50°C$, $P_f = 1$ bar, $P_d = 8$ mbar; s, shell-side feed; t, tube-side feed).

CONCLUSIONS

A homogenous oligo-PDMS^{vi} coating layer as thin as 1 μm was successfully deposited on the surface of a PVDF support membrane based on a four-step coating procedure. The results obtained from gas permeation studies and SEM examinations revealed that the coating thickness, uniformity, and integrity were affected by several factors including surface characteristics of the support membrane, duration and degree of applied vacuum, coating solution concentration, and coating solution mixing time.

TABLE IV
Operating Conditions and Separation Results of VOC/N_2 Systems

VOC	Ethyl acetate	Pentanone	Toluene
Module	2	2	3
Feed flow rate (mL/min)	100–200	100–300	60
Feed concentration (ppmv)	384–7213	~21,200	4500–30,000
Temperature (°C)	40	40	40
Removal efficiency	92–99%	~100%	98–100%

The developed PDMS^{vi}–PVDF composite membranes were then applied to separation of a wide variety of VOCs (benzene, toluene, acetone, chloroform, ethyl acetate, and pentanone). In general, the results showed that the PDMS^{vi}–PVDF hollow-fiber composite membranes that had been developed displayed very high removal efficiency (>96%) under favorable operating conditions for all the VOCs examined. The VOC removal efficiency was extremely high, above 99.9% at low feed rates at 40°C for some VOCs, such as benzene, toluene, chloroform, ethyl acetate, and pentanone. For smaller and more volatile molecules such as acetone, removal efficiency declined drastically when flow rate was increased. Also, tube-side feed operation was found to be better than shell-side feed operation in efficiency of VOC removal.

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