

Pervaporation Performance of Polyetherimide Membranes Spin- and Dip-Coated with Polydimethylsiloxane*

C. A. PAGE,¹ A. E. FOUDA,^{1,†} R. TYAGI,¹ and T. MATSUURA²

¹Institute for Environmental Chemistry, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada; and

²Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Canada K1N 6N5

SYNOPSIS

The pervaporation performance of polydimethylsiloxane (SR) spin- and dip-coated polyetherimide (PEI) membranes was investigated for acetic acid/water mixture. The spin-coating technique was used to produce a thin, uniform coating, and compared to the dip-coating technique in terms of pervaporation performance, thickness, and uniformity of the coating layer. It was found that the PEI membranes studied were water-selective and that the water selectivity of PEI membranes increased when spin-coated with a SR solution. It was also found that the water selectivity increased when the PEI membranes were coated with SR solutions of increasing concentration, although the permeate flux noticeably decreased. The coating thickness was measured by the weighing technique and the results were compared with the thickness estimation by two versions of the resistance model. It was determined that the spin-coating technique can provide a thinner and more uniform coating than the dip-coating technique, and that the coating solution penetrates the membrane pores before coating the surface. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation, the separation of liquid mixtures by vaporization through a membrane, is useful for separation of liquids with close boiling temperatures or for mixtures which lead to an azeotrope, and when a minor component is preferentially transported through a membrane.

Commercial applications of pervaporation began as recently as 1982 with the pilot plant scale dehydration of water-ethanol mixtures.¹ In general, the pervaporation processes in industry can be divided into the following groups: the dehydration of alcohols and organic solvents with membranes of hydrophilic polymers or of charged polymers, and the separation of volatile organic compounds from water with hydrophobic membranes.^{2,3}

Several studies have been carried out on the separation of acetic acid/water mixtures using pervaporation. Deng et al.⁴ studied the pervaporation of

acetic acid/water mixtures using hydrophobic and hydrophilic membranes, specifically, polydimethylsiloxane (SR), aromatic polyamide, and laminated SR-aromatic polyamide membranes. They found that SR membranes were acetic-acid selective, aromatic polyamide membranes were water-selective, and laminated membranes had further increased the water selectivity. Bai et al.⁵ investigated the separation of acetic acid/water mixtures by pervaporation using SR-coated polyetherimide (PEI) membranes. They found that the selectivity of the PEI membranes depended on the pore size of the support membrane and on the condition of the SR coating. They were able to control the performance of these composite membranes by changing the characteristics of either the coating layer or the substrate layer. In addition, an increase in the number of SR coating layers caused the pervaporation flux to decrease. The thickness of the SR coating is, therefore, an important variable affecting pervaporation performance since the application of a thinner coating layer would increase the permeate flux.

Several methods currently exist to prepare thin films, which may be applied to the preparation of

* Issued as NRCC No. 37574.

† To whom correspondence should be addressed.

thin membranes and coating layers. Nakamae et al.⁶ prepared ultrathin membranes by spreading polymer solutions, specifically, ethylene-vinyl alcohol copolymer (EVA) and ethylene-vinyl alcohol acrylic acid terpolymer, on a water surface. A simple coating technique has been used to coat polyetherimide and polyethersulfone membranes; this involves mounting a flat membrane at the bottom of a cylindrical permeation cell, pouring the coating solution into the cell, and inverting, followed by curing.^{5,7}

Many coating methods have been outlined,⁸ including physical vapor deposition (PVD), such as evaporation and sputtering methods, and chemical vapor deposition (CVD), which involves chemically reacting a volatile compound with other gases to produce a nonvolatile solid which deposits atomistically on a substrate. Other coating techniques exist, such as cathodic arc plasma deposition (CAPD), thermal chemical vapor deposition, photochemical vapor deposition, plasma-enhanced chemical vapor deposition, and sol-gel coating techniques. Sol-gel coating encompasses several processes involving a single-phase liquid or a stable suspension of colloidal particles that undergoes transition into a gel. Sol-gel coatings include all coatings applied by spinning, dipping, and draining techniques.⁹

Most sol-gel coatings are applied by dip-coating; the meniscus which develops at the interface between the coating solution and the solid substrate produces a thin film on the solid substrate as it is withdrawn from the solution. The film thickness is partially set by competition between viscous, capillary, and gravitational forces. It has been shown that film thickness increases with increasing withdrawal rate.⁹

Spiers et al.¹⁰ presented an analysis of predicting the film thickness as a function of withdrawal speed and the physical properties of the fluid. Their analysis was restricted to Newtonian liquids and have shown that the deposited film thickness (h) is that at which viscous drag and gravity are in balance.

Coatings with thicknesses of 50–500 nm may be obtained by the dip-coating technique. Thicker coatings can be obtained by repeated dipping; however, peeling often occurs when drying these successive coatings.⁹ Also, if the coating solution evaporates too quickly, the viscosity of the coating rises and prevents uniform thinning.

Spin-coating is the most common method of applying uniform, thin coatings on many types of workpieces. The technique can lead to very uniform films of precisely controlled thickness. Levinson et al.¹¹ found that the film thickness produced by this

technique is greatly affected by the following process parameters:

1. spinning rate
2. total spinning time
3. density and viscosity of the solution
4. concentration of the solution
5. volatility of the solvent

Roux and Paul¹² have prepared multilayer composite membranes for gas separation, using the spin-coating process. They studied the performance characteristics in terms of the effects of spinning speed, the coating solution concentration, and the number of selective layers coated onto the substrate material.

Bornside et al.¹³ divided the spin-coating process into four stages: deposition, spin-up, spin-off, and evaporation. The first stage (deposition) involves applying an excess amount of coating solution to the substrate membrane. In the second stage (spin-up), the centrifugal forces generated by spinning the substrate cause the coating to flow radially outwards. In third stage (spin-off), the excess coating solution forms droplets and spins off the substrate membrane. The flow of the coating solution begins to slow down as the thickness decreases because the resistance to flow increases, and evaporation raises viscosity until evaporation becomes the only mechanism for film thinning. Evaporation, which is the last stage, causes thinning of the coating layer.

Meyerhofer¹⁴ presented a model based on the work of Emslie et al.¹⁵ for the description of the thin films prepared from solutions by spinning. At the start, a layer of polymer solution of uniform thickness (h_0) is applied on horizontal circular surface of the substrate. At time 0, the substrate is spun at a radial spin rate ω and the resulting layer tends to be of uniform thickness because of two competing forces: the centrifugal force which drives the coating solution radially outward and the viscous force which acts radially inward.

Emslie et al.¹⁵ have shown that for a Newtonian solution, when there is no evaporation (no change in the viscosity μ), the coating thickness profile remains uniform at all times and decreases with time according to the equation:

$$h(t) = \frac{h_0}{\sqrt{1 + 4\rho\omega^2 h_0^2 t / 3\mu}} \quad (1)$$

Despite the profile at deposition, the coating film tends towards uniformity by the spin-off stage. Scriven¹⁶ has shown that for coating solution vis-

cosities between 0.001 and 0.1 Pa·s, and with angular velocities from 3,000 to 8,000 rpm, the amount of time required to thin a nonuniform film from 1 mm to a uniform thickness of 1 μm is between a few seconds and a few minutes.

Many techniques exist to determine thin film thickness, which may be divided into optical and mechanical techniques. Optical methods for thin film thickness determination include fringes of equal thickness (FET), fringes of equal chromatic order (FECO), variable angle monochromatic fringe observation (VAMFO), and constant angle reflection interference spectroscopy (CARIS).⁸ Mechanical techniques include weight measurement, which was used in this work, the stylus profilometry, and crystal oscillator methods.⁸

Methods for structural characterization include scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction techniques, among others. This characterization includes the identification of surface and interior atoms and compounds, as well as their spatial distributions.

The objectives of this work are to use the spin-coating technique to produce a thin film of uniform thickness; to evaluate the performance of spin-coated membranes using pervaporation of an acetic acid/water mixture; to estimate the thickness of the coating; and to compare spin-coating with dip-coating techniques in terms of pervaporation performance, thickness, and uniformity of the coating.

EXPERIMENTAL

Materials

Polyetherimide polymer, or Ultem, was supplied by General Electric Co., and the backing material used was a polyester film, style 3396, supplied by Filtration Science Co. The solvent N-methylpyrrolidone, supplied by J. T. Baker Co., was used as provided. Glacial acetic acid (assay 99.7% min) from Anachemia was used for pervaporation feed. The coating solution was prepared, following directions provided, using Sylgard 184 silicone elastomer and curing agent supplied by Dow Corning Corporation, and diluted in hexane provided by BDH Inc.

Preparation of Polyetherimide Membranes

Preparation of Polymer Casting Solutions

Polyetherimide polymer (Ultem 1000), was dried at 150°C for 4 h. The polymer was cooled to room tem-

perature in a desiccator for at least 2 h. In a dry box, approximately 40 g of the Ultem was weighed into glass reagent bottles for each casting solution. Appropriate amounts of the solvent N-methylpyrrolidone (NMP) were then added to prepare 20%, 23%, 25%, and 27% by weight solutions of Ultem in NMP. The bottles were adequately sealed and were placed on a rolling rack for 7 days to allow the polymer to dissolve completely. Casting solutions were then filtered using polyester cloth filters in a 47-mm diameter stainless-steel pressure holder, from Millipore Corporation. Nitrogen gas was used to pressurize the solutions through the filter. The reagent bottles were left for 2–3 days so that the dissolved air was removed from the solutions.

Preparation of Substrate Polyetherimide Membranes

The cold gelation bath was prepared before the membranes were cast, by mixing distilled water with ice chips in a container, and leaving for 10 minutes. The water was then filtered by a wire mesh into a plastic receptacle. Glass casting plates were cleaned and dried thoroughly.

A piece of polyester backing material, approximately 35 cm \times 45 cm, was taped to the casting plate using double-sided adhesive tape. The casting plate was then secured by placing a metal plate at one end. The filtered casting solution was cast (casting thickness 10 mils = 2.54×10^{-4} m, adjusted by a casting knife) onto the backing sheet. Immediately after casting, the membrane and casting plate were immersed in the cold bath using a quick, smooth motion.

The membrane sheet was left in the cold bath for at least 1 h, then was examined for pinholes and flaws. Coupons with an area of 10.18 cm² were outlined using a circular die and cutout.

The wet membrane coupons were immersed in ethyl alcohol bath for 6 h to exchange the water. The ethyl alcohol was then replaced with a fresh batch of ethyl alcohol and the membranes were immersed for 16 h. The solvent was then replaced with hexane as a second solvent and the membranes were immersed for 24 h. After the solvent exchange, the membranes were air-dried in a desiccator for at least 24 h before use.

Preparation of Coated Polyetherimide Membranes

The silicone rubber coating solutions (SR) were prepared from the commercial elastomer product

called Sylgard 184. The silicone elastomer was supplied in two parts: a lot-matched base and a curing agent. The coating solution was prepared by thoroughly mixing the base material and the curing agent in a 10 : 1 by weight ratio. The mixing was done using a smooth action to minimize the introduction of excess air to the solution. The mixture was then diluted in hexane to a specific concentration.

In the dip-coating method, a dry PEI membrane was mounted at the top of a glass jar. The membrane surface was dipped into the SR solution for 1 min, then was removed from the coating solution and left in the air to drain the excess solution. The coating solution was then evaporated for 5 min and cured in the oven at 80°C for 1 h.

In the spin-coating method, the equipment shown in Figure 1 was used as follows:

- A dry PEI membrane was mounted on a circular glass plate and was secured using double-sided tape.
- The glass plate was fitted to the shaft of a magnetic stirrer; 5 ml silicone rubber solution was poured onto the membrane, which was spun at 550 rpm for 5 min.
- The thin film produced was cured at 80°C for 1 h.

Pervaporation Experiments

The experimental apparatus is shown in Figure 2. The PEI membrane was mounted in a static cell, similar to those used in reverse osmosis and ultra-filtration experiments and described elsewhere in detail.¹⁷ About 50 mL of feed solution was loaded into the cell. The vacuum pump was started and the permeate was collected in the collection trap immersed in liquid nitrogen. After a stable permeation rate was reached after about 60 min, the permeate was switched to the second cold trap. The product was collected for some time; then the valve of the cold trap was closed and the trap was removed, sealed, and was allowed to reach room temperature. The permeation rate was measured by weighing the cold trap filled with the product. The permeate was then analyzed using a Shimadzu gas chromatograph GC-8A equipped with a thermal conductivity detector having 1.80 m column packed with chrom-P 80 : 100 mesh.

Gas Permeation Experiments

The dry membrane to be tested was installed in a cylindrical gas permeation cell. Nitrogen gas was

passed through the membrane, and both the volumetric flow rate of the gas (measured by a bubble flow meter) and the upstream pressure were noted.

Thickness Estimate by Weight Measurement

Silicone rubber coating thickness was estimated by weight measurement. The weights of the uncoated and coated membranes were noted, knowing the density of cured silicone rubber, area coated, and the weight difference; the coating thickness was calculated.

Contact Angle

The contact angle between water and a membrane was determined by placing a drop of water on the membrane surface and measuring the angle directly through a microscope fitted with a protractor. Additional equipment required was a lamp to illuminate the specimen, a Variac transformer to control the light intensity, a lab jack to hold the specimen in front of the microscope, a syringe to deposit a small bead of water, and double-sided tape to hold down the membrane.

RESULTS AND DISCUSSION

Pervaporation

Pervaporation experiments were carried out on uncoated polyetherimide (PEI) membranes with 0.20 mol fraction acetic acid in water as a feed solution. Acetic-acid mol fraction in the permeate and the permeate flux were measured, and the results are shown in Table I and Figure 3. Permeate flux decreased nonlinearly, approximately 25 times, as PEI concentration in the casting solution increased from 20 to 27 wt %. The acetic-acid mol fraction in the permeate also decreased as PEI concentration increased, indicating that the pore size was reducing, but all the membranes were water-selective.

Another set of pervaporation experiments was carried out on PEI membranes spin-coated with a 50 wt % silicone rubber in hexane solution; the experimental results are also shown in Table I and Figure 3. Permeate flux increased slightly when the PEI concentration increased from 20 wt % to 23 wt %, then decreased as the PEI concentration increased from 23 wt % to 27 wt %. On the other hand, the acetic-acid mol fraction in permeate decreased from 0.098 to 0.0041 as the PEI concentration increased from 20 wt % to 27 wt %.

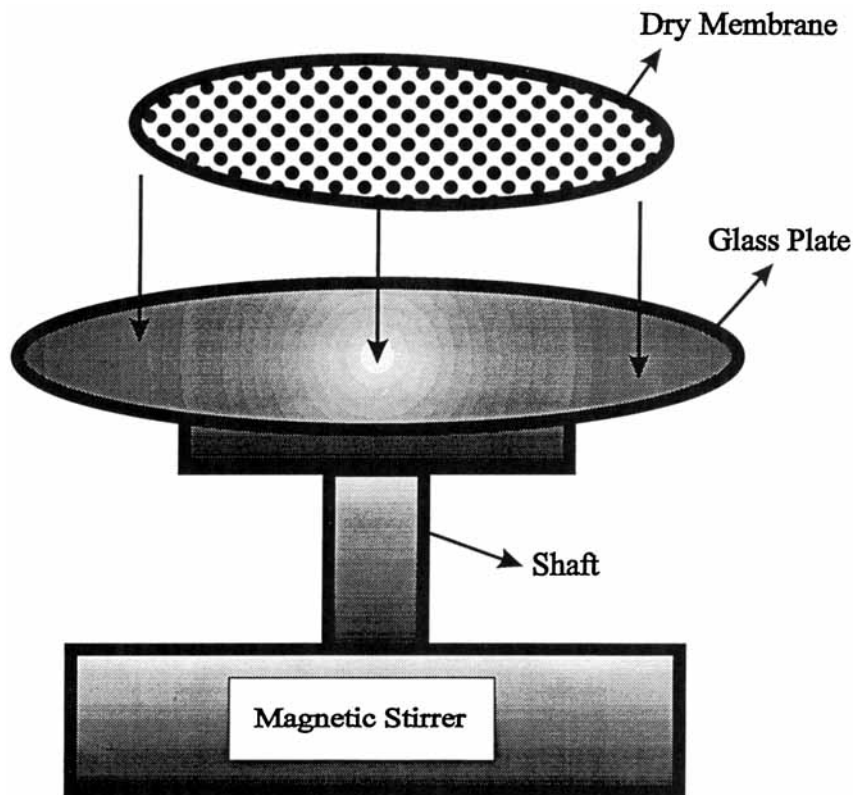


Figure 1 Diagram of spin-coating equipment.

The separation factor, α , results are shown in Table II for different PEI concentrations. A dramatic increase in the separation factor is shown for all concentrations; however, as the PEI concentration increased, the separation factor ratio of the coated to the uncoated membranes increased dramatically from 2.13 to 33.19 as the PEI concentra-

tion in the casting solution increased from 20 wt % to 27 wt %. It is clear that the coating has increased the water selectivity of the membranes for all PEI membranes; however, the effect is stronger for membranes with smaller pore sizes which are prepared from casting solutions containing higher concentration of the polymer material.

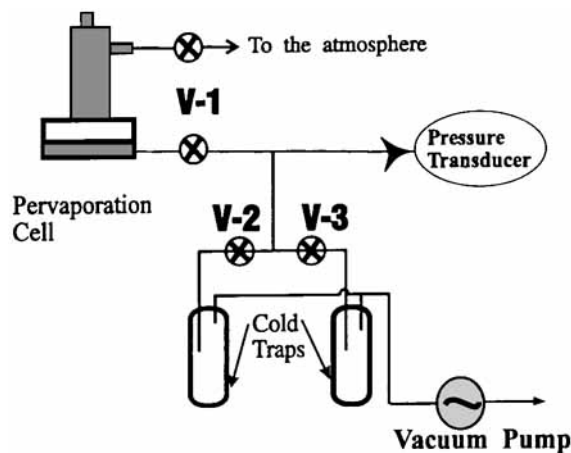


Figure 2 Schematic diagram for pervaporation experiments.

The effect of the SR concentration on the pervaporation performance of the PEI membranes was studied by using substrate membranes prepared from casting solutions containing a 25 wt % PEI concentration. The substrate membranes were spin-coated with various solutions of silicone rubber diluted in hexane to concentrations of 0.5, 2, 7.5, 15, 30, 50, and 70 wt %. The pervaporation experiments were conducted using acetic-acid feed solution of 0.2 mol fraction. The effect of silicone rubber concentration on the permeate flux and composition is shown in Table III and Figure 4. As the concentration of the SR (silicone rubber) increased in the coating solution, the permeate flux decreased non-linearly. At very low SR concentration of 0.5 wt %, the coating did not effectively cover the membrane surface. Consequently, the values of the acetic-acid mol fraction in the permeate as well as the permeate

Table I Pervaporation of Uncoated and Spin-Coated PEI Membranes

PEI Conc in Substrate Membrane wt %	Uncoated Membranes		Spin-Coated Membranes	
	Permeate Flux $\times 10^4$, mol/m ² ·s	Acetic-Acid mol Fraction in Permeate	Permeate Flux $\times 10^4$, mol/m ² ·s	Acetic-Acid mol Fraction in Permeate
20	495.0	0.188	9.79	0.0980
23	178.0	0.191	16.4	0.0310
25	37.3	0.153	99.8	0.0090
27	17.7	0.120	47.4	0.0041

SR concentration in coating solution = 50 wt % in hexane; feed = 0.20 acetic-acid mol fraction.

flux did not change very much from the values of the uncoated membranes.

When the membrane was coated with a 2 wt % SR solution, both acetic-acid mol fraction in the permeate and the permeate flux decreased dramatically to reflect the effect of coating. However, the permeate composition remained relatively constant as the SR concentration increased from 2 wt % to 70 wt %. This indicates that the spin-coating technique is very effective at low SR concentrations in the coating solution; however, the performance does not improve by increasing the SR concentration in the coating solution. It is logical to assume that by increasing the SR concentration in the coating solution, the coating thickness would increase accordingly. However, the performance of the membranes coated with higher SR concentrations can be compared to the performance of the multiple coated membranes. Bai et al.⁵ found that when the number of SR coatings increased, the water selectivity increased significantly after the first coating, and then leveled off despite subsequent coating applications.

Pervaporation experiments were also performed using 25 wt % PEI membranes dip-coated with 2, 7.5, 15, and 30 wt % SR coating solution. These

results are given in Table IV and shown in Figure 4 with the results of the spin-coated membranes. Similar to the spin-coated membrane results, the permeate flux and acetic-acid mol fraction in the permeate decreased with increasing coating solution concentration. Both permeate flux and acetic-acid mol fractions were greater than the corresponding values when the membranes were spin-coated with solutions of the same SR concentrations.

Coating Thickness Estimation by Gas Permeability

Gas permeability experiments were carried out using nitrogen gas on 20, 23, 25, and 27 wt % PEI membranes. The results are given in Figure 5(A) and Table V. Permeability decreased with increasing PEI concentration, indicating that the membrane pore size decreased as PEI concentration increased. These permeability results were used, as shown in the next section, to calculate the resistance of the substrate membrane for nitrogen permeation and to estimate the coating layer thickness.

Gas permeability experiments were also carried out using nitrogen gas on 25 wt % PEI membranes spin-coated with various concentrations of SR: 2,

Table II Separation Factor α , for Uncoated and Coated PEI Membranes

PEI Conc in Substrate Membrane, wt %	Separation Factor (α) for		
	Uncoated Membrane	Spin-Coated Membrane	Ratio α (Coated/ α (Uncoated))
20	1.08	2.30	2.13
23	1.06	7.78	7.34
25	1.38	27.47	19.91
27	1.83	60.73	33.19

SR concentration in coating solution = 50 wt % in hexane; feed = 0.20 acetic-acid mol fraction.

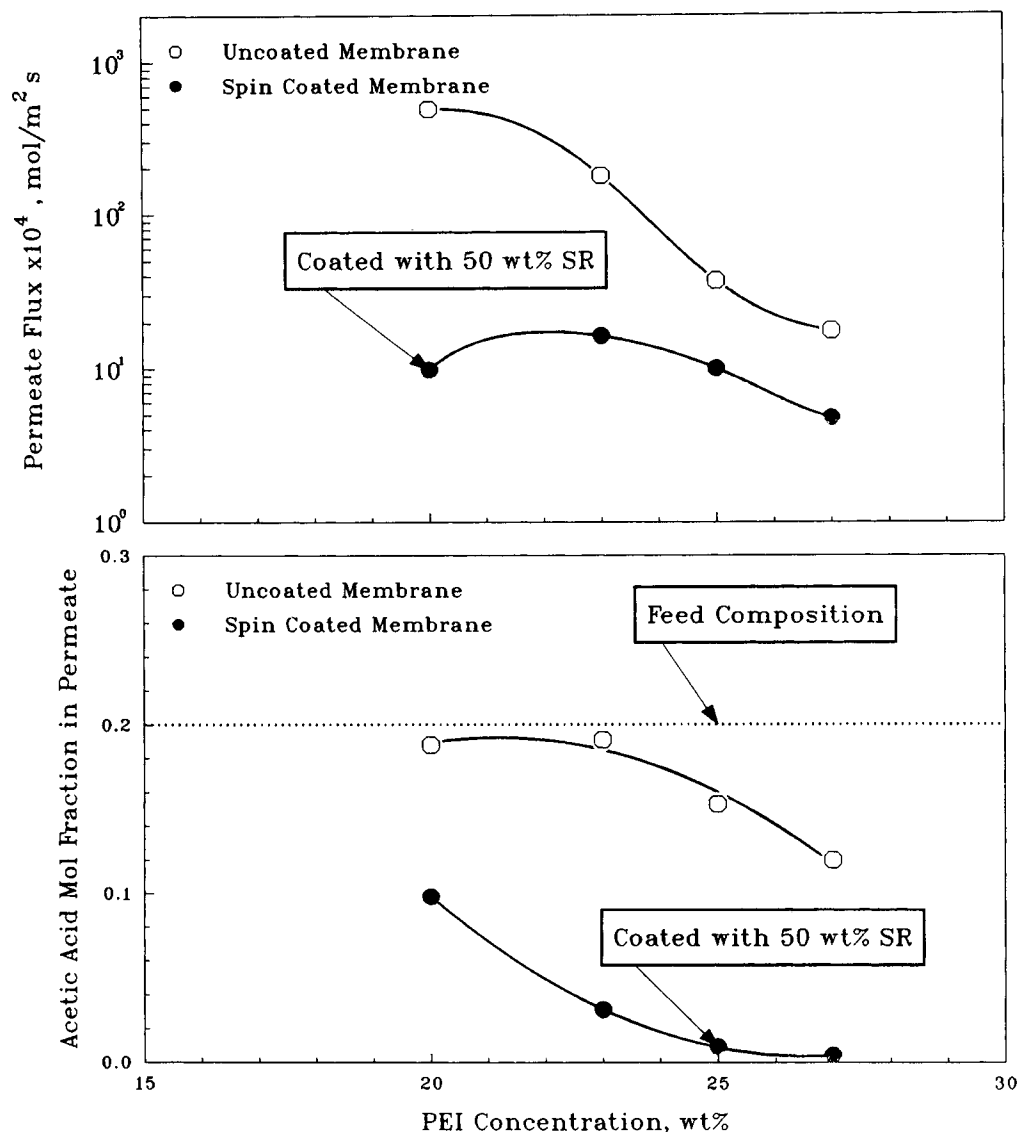


Figure 3 Effect of polymer concentration on the pervaporation performance of coated and uncoated membranes. (Feed = 0.2 mol fraction acetic acid.)

7.5, 15, and 30 wt %. The same gas permeability experiments were also carried out on the dip-coated membranes with solutions having SR concentrations of 2, 7.5, 15, and 30 wt %. The results of the nitrogen gas permeability vs the concentration of SR in hexane (wt %), are shown in Figure 5(B) and are given in Table VI.

The thickness of the coating layer can then be calculated by using the resistance model approach which was developed by Henis and Tripodi.¹⁸⁻²⁰ Chen et al.⁷ and Fouda et al.²¹ discussed the model in detail when they used it to analyze their experimental data for gas permeation through silicone-coated and

laminated polyethersulfone membranes. The next section shows the procedure to calculate the thickness of the coating layer using the resistance model approach.

Resistance Model I

Figure 6(A) shows the schematic diagram for this approach. It is assumed that the coating layer will not penetrate the substrate and thus forms a layer on the top of the membrane with a thickness δ . The resistances of the coating layer and the substrate membrane are in series, and the thickness of the SR layer is calculated as follows:

Table III Effect of SR Concentration in Coating Solution on the Pervaporation of Spin-Coated PEI Membranes

SR Conc wt %	Permeate Flux $\times 10^4$, mol/m ² ·s	Acetic-Acid mol Fraction in Permeate	Separation Factor, α
0	37.3	0.153	1.38
0.5	24.1	0.108	2.06
2	12.0	0.0223	10.96
7.5	10.4	0.0204	12.00
15	8.96	0.0195	12.57
30	7.70	0.0251	9.71
50	9.49	0.0120	20.58
70	5.40	0.031	7.81

PEI substrate prepared from 25 wt % polymer solution; feed = 0.20 acetic-acid mol fraction.

- From the gas permeation data for the uncoated PEI membrane (the pressure difference, Δp_{PEI} , and the gas flow rate, Q_{PEI} , mol/s) the resistance of the PEI membrane, R_{PEI} , may be calculated by:

$$R_{PEI} = \frac{\Delta p_{PEI}}{Q_{PEI}} \quad (2)$$

- Similarly, the resistance of the coated membrane, R_{TOTAL} may be calculated by

$$R_{TOTAL} = \frac{\Delta p_{TOTAL}}{Q_{TOTAL}} \quad (3)$$

where Δp_{TOTAL} is the pressure difference and Q_{TOTAL} is the gas flow rate for the coated membrane. The resistance of the SR layer is given by:

$$R_{SR} = R_{TOTAL} - R_{PEI} \quad (4)$$

- the thickness of coating layer is then given by:

$$\delta_{SR} = R_{SR} \times P_{SR} \times A \quad (5)$$

where R_{SR} , P_{SR} , and A are the resistance of the SR layer, the intrinsic permeability of the silicone film for the nitrogen gas which is known to be 1.842×10^{-13} mol/m²·s·Pa [= 250×10^{-10} ·cm³ (STP)·cm/cm²·s·cmHg]²² and the area of membrane tested (10.18 cm²), respectively.

Table IV Effect of SR Concentration in Coating Solution on the Pervaporation of Dip-Coated PEI Membranes

SR Conc wt %	Permeate Flux $\times 10^4$, mol/m ² ·s	Acetic-Acid mol Fraction in Permeate	Separation Factor, α
0	37.3	0.1530	1.38
2	25.2	0.1245	1.76
7.5	10.1	0.0208	11.77
15	15.6	0.0312	7.76
30	6.7	0.0348	6.93

PEI substrate prepared from 25 wt % polymer solution; feed = 0.20 acetic-acid mol fraction.

Resistance Model II

Figure 6(B) shows the schematic diagram of this more realistic approach with the following assumptions:

- The coating layer is assumed to penetrate into the voids of the porous substrate membrane; hence, the resistance of the voids cannot be neglected, as in resistance model I.
- The resistance of the substrate membranes is composed of two resistances in parallel: mainly, R_2 of the PEI matrix and R_3 of the voids.
- At a certain minimum concentration of the SR solution, we assume that all the coating solution has penetrated the substrate membrane; hence, the composite resistance R_{MIN} , is the new substrate resistance which will be in series with the resistance of coating layer at higher SR concentrations.
- At higher SR concentration, a top coating layer is formed with thickness $\delta_1 < \delta$, due to pene-

Table V Gas Permeation for Uncoated PEI Membranes

PEI Conc in Substrate Membrane, wt %	Flow Rate, mL/min	Permeability $\times 10^9$, mol/m ² ·s·Pa
20	139.5	362.0
23	94.6	245.0
25	67.1	174.0
27	15.6	40.4

Gas = nitrogen, temperature = 23°C, and feed pressure = 276 kPa (g).

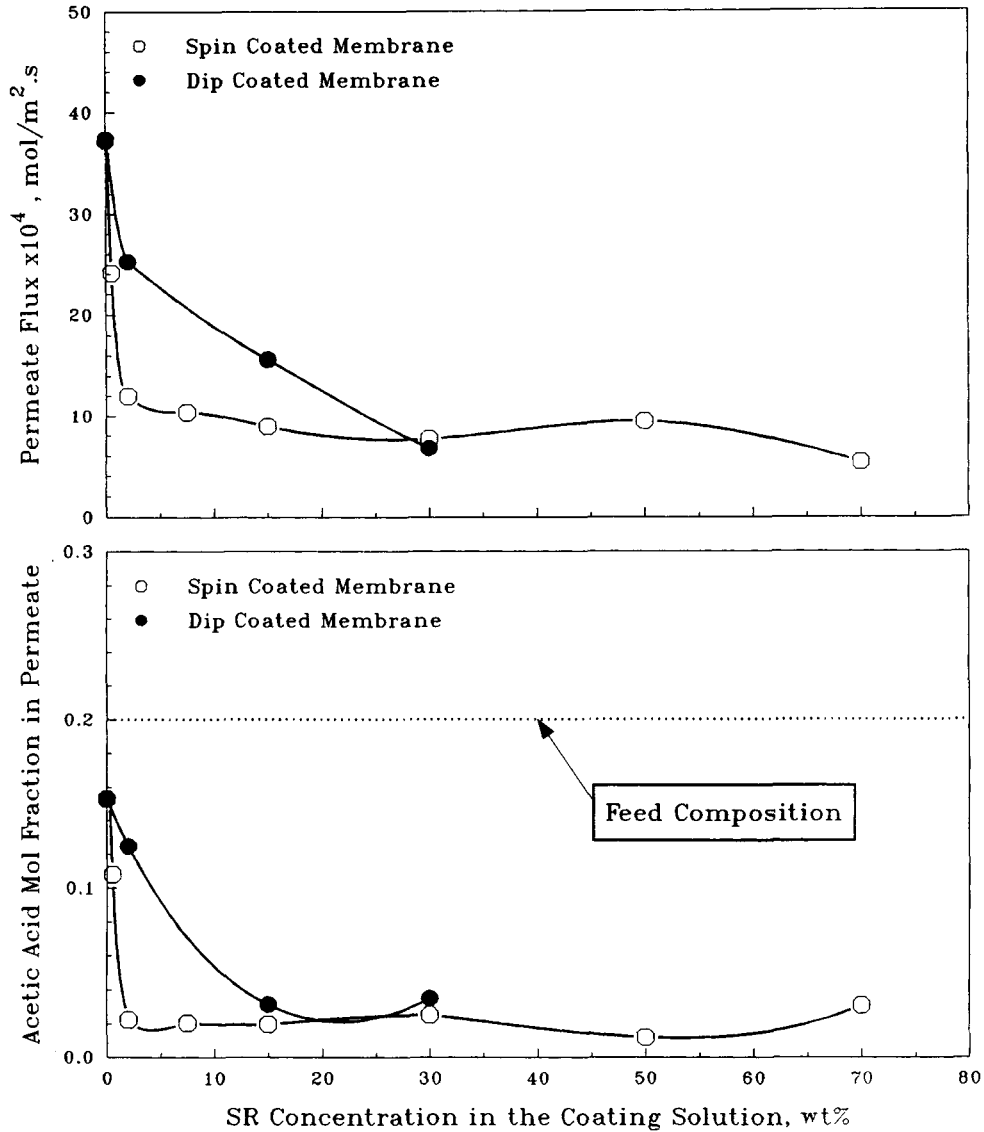


Figure 4 Effect of SR concentration in the coating solution on the pervaporation performance of the spin- and dip-coated PEI support membranes. (PEI substrate was prepared from a 25 wt % polymer solution.)

tration of the SR solution in the membrane. In this case, the resistance of the composite membrane is treated as being partially in series and partially in parallel.

The resistance and the thickness of the SR layer are calculated as follows:

- The resistance of the uncoated PEI membrane given by eq. (2) is the combination of R_2 , the resistance of the PEI polymer matrix, and

$(R_3)_{un}$, the resistance of unfilled pore space, in parallel, as shown in Figure 6 (B). Therefore,

$$R_{PEI} = 1 / \left[\frac{1}{R_2} + \frac{1}{(R_3)_{un}} \right] \quad (6)$$

- Similarly, the resistance of the membrane coated with the minimum amount of effective coating, R_{MIN} , which would be enough to penetrate the pores but with negligible thickness (i.e., $R_1 = 0$), may be calculated by:

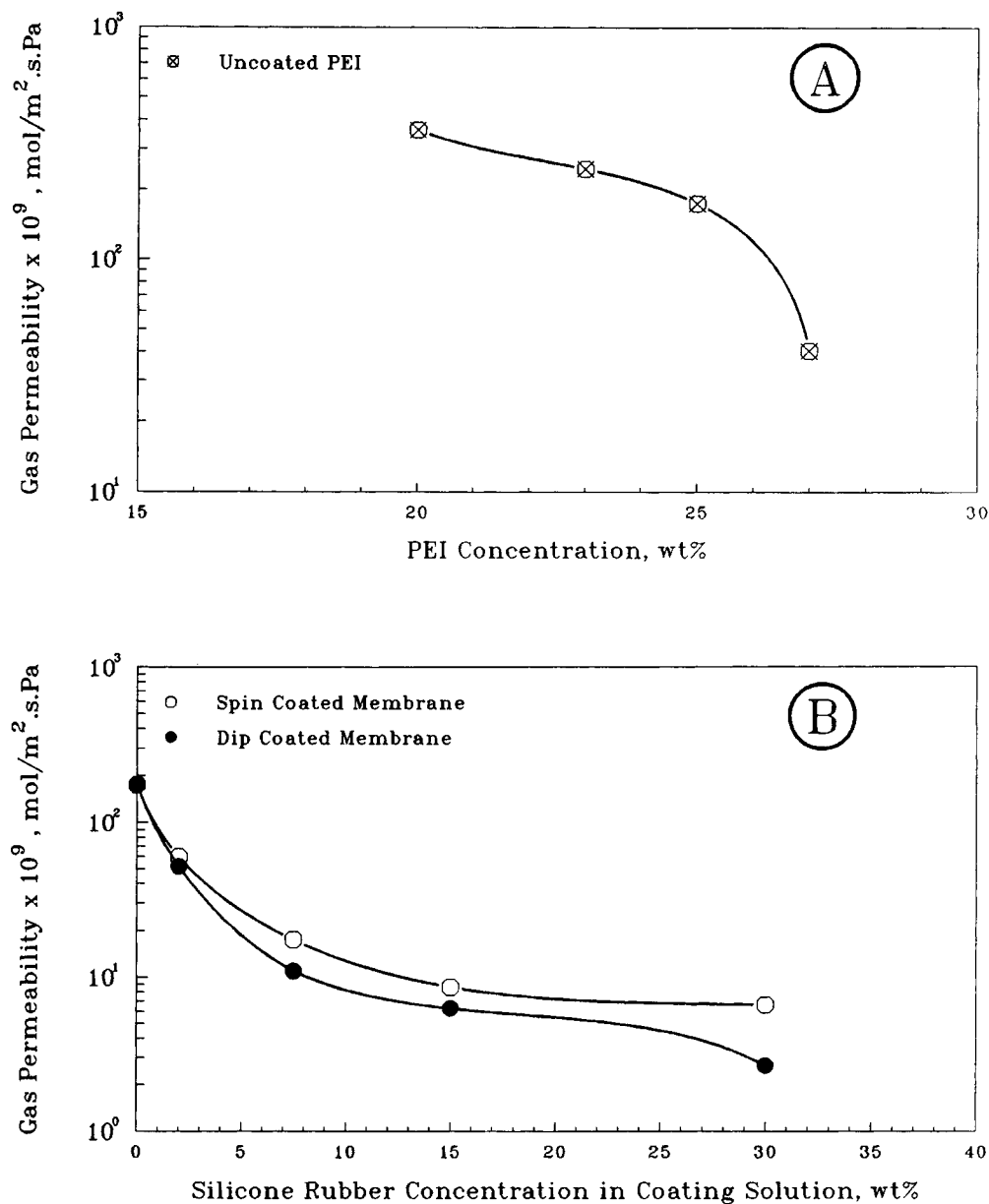


Figure 5 Gas permeability through (A) uncoated and (B) coated PEI support membranes. (PEI substrate was prepared from a 25 wt % polymer solution.)

$$R_{MIN} = \frac{\Delta p_{MIN}}{Q_{MIN}}$$

$$= 1 / \left[\frac{1}{R_2} + \frac{1}{(R_3)_{fill}} \right] \quad (7)$$

where $(R_3)_{fill}$ is the resistance of the void filled with silicone rubber. R_{MIN} is chosen arbitrarily as the resistance of the PEI membrane coated with 2 wt % SR solution.

- The total resistance for the membrane coated with SR solutions of higher concentrations is given by:

$$R_{TOTAL} = \frac{\Delta p_{TOTAL}}{Q_{TOTAL}}$$

$$= 1 / \left[\frac{1}{R_2} + \frac{1}{(R_3)_{fill}} \right] + R_1 \quad (8)$$

Note that a SR layer formed on the top of the

Table VI Gas Permeation for Coated 25 wt % PEI Membranes

SR Conc wt %	Flow Rate, mL/min		Permeability $\times 10^9$, mol/m ² ·s·Pa	
	Spin-Coated	Dip-Coated	Spin-Coated	Dip-Coated
0	67.1	67.1	174.0	174.0
2	23.0	19.9	59.6	51.6
7.5	6.71	4.22	17.4	10.9
15	3.33	2.41	8.6	6.3
30	3.54	1.02	6.6	2.6

Gas = nitrogen, temperature = 23°C, and feed pressure = 276 kPa (g).

substrate membrane and its resistance, R_1 , contributes to the total resistance in series.

- The thickness of the top coating layer can then be calculated by

$$\delta_1 = R_1 \times P_{SR} \times A \quad (9)$$

where P_{SR} is the intrinsic permeability of the silicone film for the particular gas used and A is the surface area of membrane tested, respectively.

Coating Thickness Estimation

The weighing method was used to estimate the coating thickness for the spin-coated membranes (0.5, 2, 7.5, 15, 30 wt % SR coatings), and the results are shown in Figure 7(A) and are given in Table VII. As expected, the thickness of the coating layer increased with the increase in the concentration of the SR in the coating solution. The coating layer thickness was also estimated by using the two resistance models outlined in the previous section. The results are also given Table VII and shown in Figure 7(A). The trend is basically similar to that obtained by the weighing method.

Figure 7(A) shows also that the thickness estimated by resistance model I is higher than that estimated by resistance model II, in which the thickness is corrected for the amount of material penetrated through the porous structure of the substrate.

The coating thicknesses of the membranes dip-coated with solutions having different SR concentrations (2, 7.5, 15, 30 wt % SR) were also estimated using the weighing method and the resistance models I and II. Table VIII and Figure 7(B) show these results.

The thickness of the coating layer increased as the concentration of the SR in the coating solution

increased. However, the agreement between the results obtained from the weighing method and the values obtained from applying the resistance models

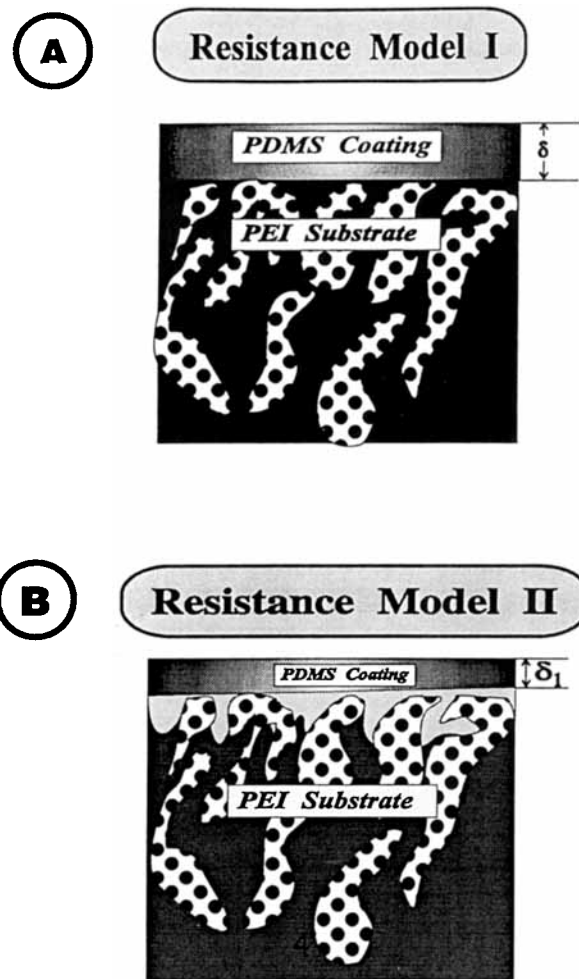


Figure 6 Schematic diagram for resistance models I and II.

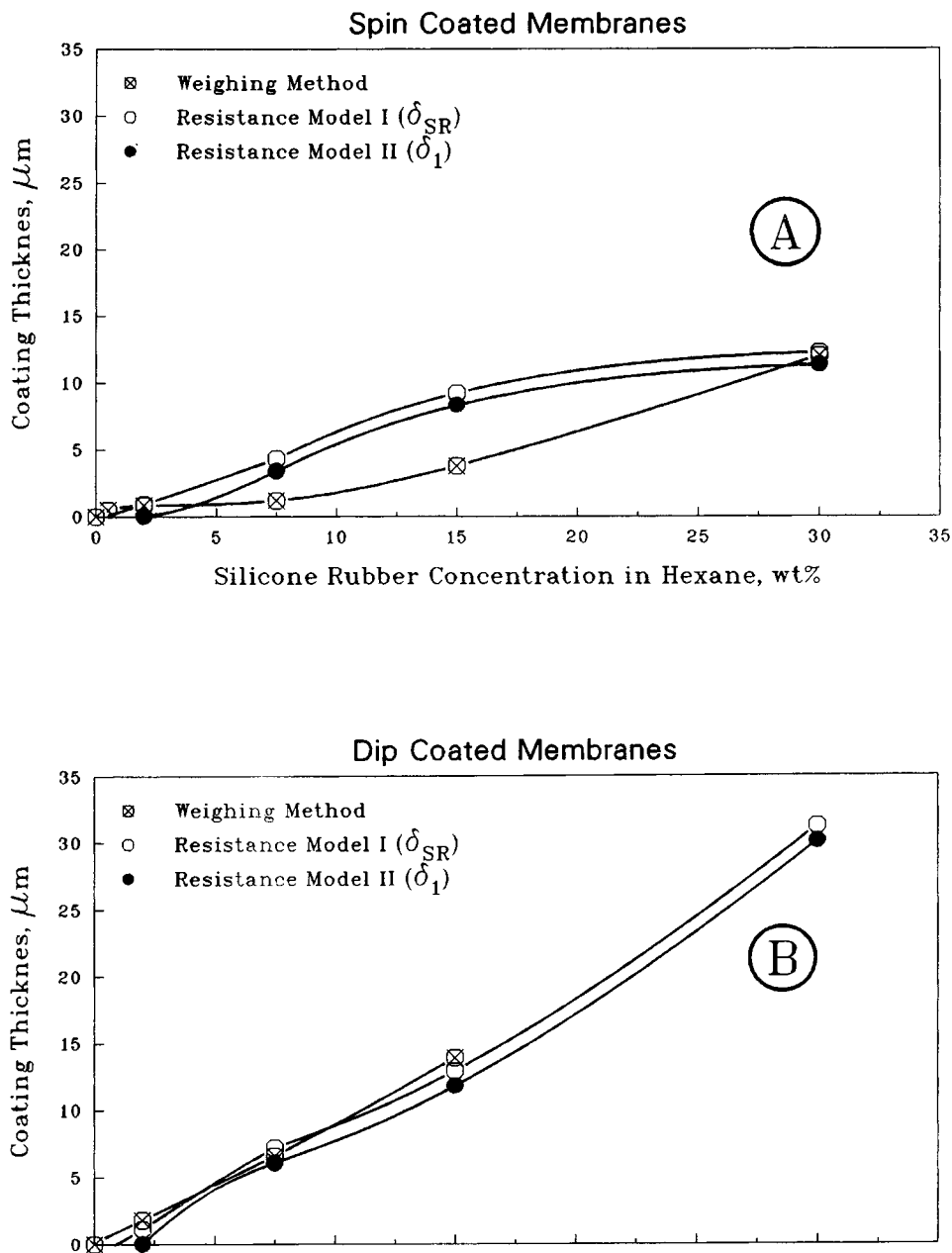


Figure 7 Thickness estimation for the (A) spin- and (B) dip-coated membranes. (PEI substrate was prepared from a 25 wt % polymer solution.)

was much closer than that for the spin-coated membrane. This can be attributed to the level of the experimental error involved in the weighing technique, which is more severe for lower values of coating thicknesses obtained by the spin-coating technique.

Structural Characterization of Membranes

Scanning electron microscopy (SEM) was used to investigate three membranes: (i) uncoated 25 wt %

PEI, (ii) 25 wt % PEI spin-coated with 2 wt % SR solution, and (iii) 25 wt % PEI spin-coated with 15 wt % SR solution. The SEM results are shown in Figures 8–10 at two different magnifications. Figure 8 shows the asymmetric structure of the uncoated membrane at magnification of $\times 500$ and $\times 5,000$. As expected, both micrographs show the substrate porous structure which is covered with undetected thin skin layer. Figure 9 shows the structure of the mem-

Table VII Thickness Estimates for Spin-Coated 25 wt % PEI Membranes

SR Conc (wt %)	Thickness Estimate (μm)		
	Weighing Method	Resistance Model I	Resistance Model II
2	0.85	0.92	0.0
7.5	1.2	4.3	3.4
15	3.8	9.2	8.3
30	12	12.2	11.3
50	18	8.7	7.8
70	—	26.4	25.5

brane spin-coated with a solution containing 2 wt % SR. Both micrographs show that the structure of this membrane is similar to the structure of the uncoated membrane shown in Figure 9, since the coating layer cannot be detected. These micrographs clearly support the assumption that all the coating solution with a 2 wt % SR concentration would penetrate the porous structure of the membrane and, hence, does not form a coating layer on top of the skin layer.

Figure 10 shows the micrographs for the membrane spin-coated with a 15 wt % SR. The SR coating on the surface of the membrane can be clearly seen. The thickness estimate of the 15 wt % coating, provided by SEM, was 0.6 μm . The thickness estimates by weighing and resistance model methods have been shown in Table VII to be 3.8, 9.2, and 8.3 μm , respectively. The large difference between these results suggests that the penetration of coating solution into the substrate voids is much more than we have thought, and the assumption of 2 wt % SR solution as sufficient to fill the membrane voids was extremely underestimated. Accordingly, both the weighing technique and the resistance model II ov-

Table VIII Thickness Estimates for Dip-Coated 25 wt % PEI Membranes

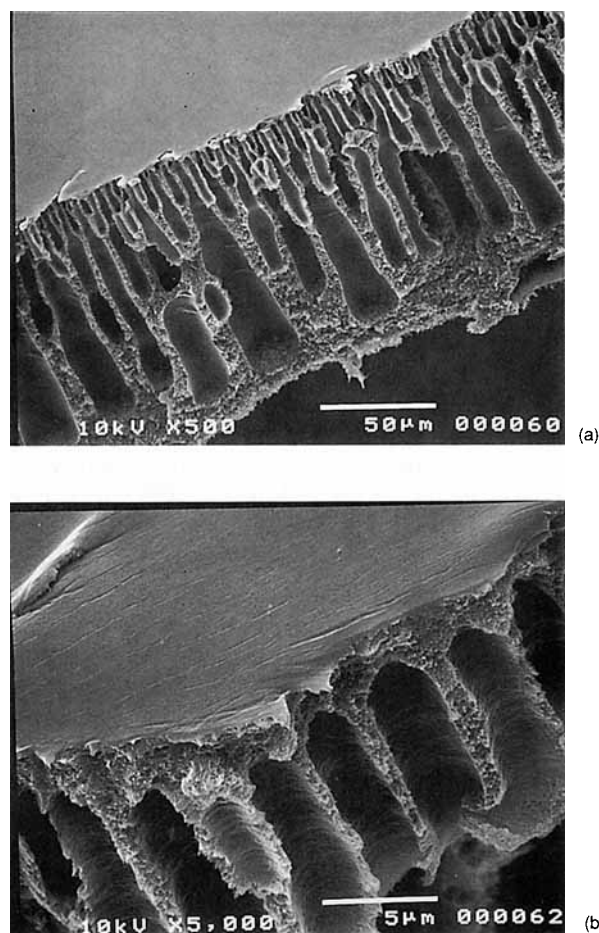
SR Conc (wt %)	Thickness Estimate (μm)		
	Weighing Method	Resistance Model I	Resistance Model II
2	1.77	1.14	0.0
7.5	6.60	7.20	6.06
15	13.96	12.91	11.77
30	46.14	31.23	30.09

erpredicted the coating thickness when compared with the micrographs in Figure 10.

Coating Technique Comparison

The spin- and dip-coating methods were compared in terms of pervaporation results, thickness estimation, gas permeability, and contact angle. Comparison of pervaporation separation factor, α , for both methods are given Tables V and VI. Only the separation factor for the 25 wt % PEI membranes spin-coated with 2 wt % SR is much greater than for the dip-coated membrane with the same coating solution. However, at SR concentrations of 7.5, 15, and 30 wt %, the values of the separation factors are closer, with the spin-coated membranes having slightly higher values.

Tables V and VI show that the permeate fluxes for the membranes dip-coated with 2 and 15 wt %


Figure 8 SEM of uncoated membrane, 25 wt % PEI: (A) magnification $\times 500$; (B) magnification $\times 5,000$.

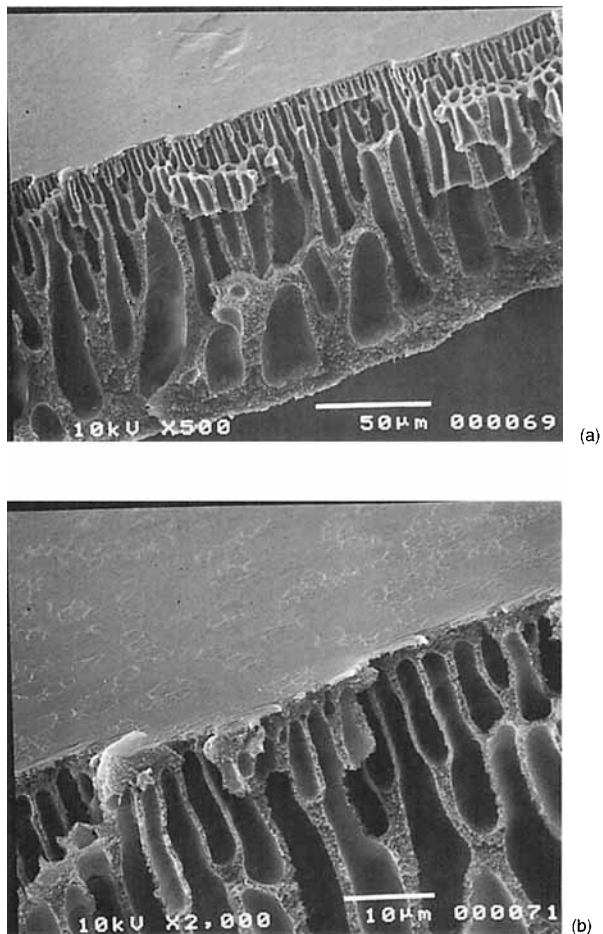


Figure 9 SEM of spin-coated membrane, 25 wt % PEI spin-coated with 2 wt % SR: (A) magnification $\times 500$; (B) magnification $\times 5,000$.

SR solutions were 2.1 and 1.74 times greater than the permeate fluxes for the spin-coated membranes, respectively. However, 30 wt % SR spin-coated membranes had higher permeate flux and acetic acid separation than the membranes dip-coated under the same conditions.

The thicknesses of the dip-coating layers, determined by using the weighing method, are between 2.1 and 5.5 times greater than the spin-coating thicknesses when the coating was made with a coating solution of the same SR concentration. The difference in coating thicknesses between coating methods was supported by visual observations made during coating procedures.

The substantial difference in thickness agrees with the higher permeability of nitrogen in the spin-coated membranes which had nitrogen permeabilities between 1.25 and 13.9 times greater than dip-coated membranes.

The contact angle between water and membrane surface was determined for 25 wt % PEI membranes uncoated and spin-coated with 2 and 15 wt % SR. The measured contact angles were 67.9° , 96.3° , and 100.3° , respectively. Contact angles, measured for 25 wt % PEI membranes dip-coated with 2 and 15 wt % SR solution were 98.1° and 100.7° , respectively. The contact angle between water and the SR surface, for the 1 mil (2.54×10^{-5} m) SR membrane (supplied by General Electric Co.), was measured as 106.25° . The contact angles for both the dip- and spin-coated membranes approached the value of the SR membrane more closely than the uncoated membranes, suggesting that the surface is most like SR. However, the differences between the spin- and dip-coated contact angle results are very small, and the difference could be within the experimental error.

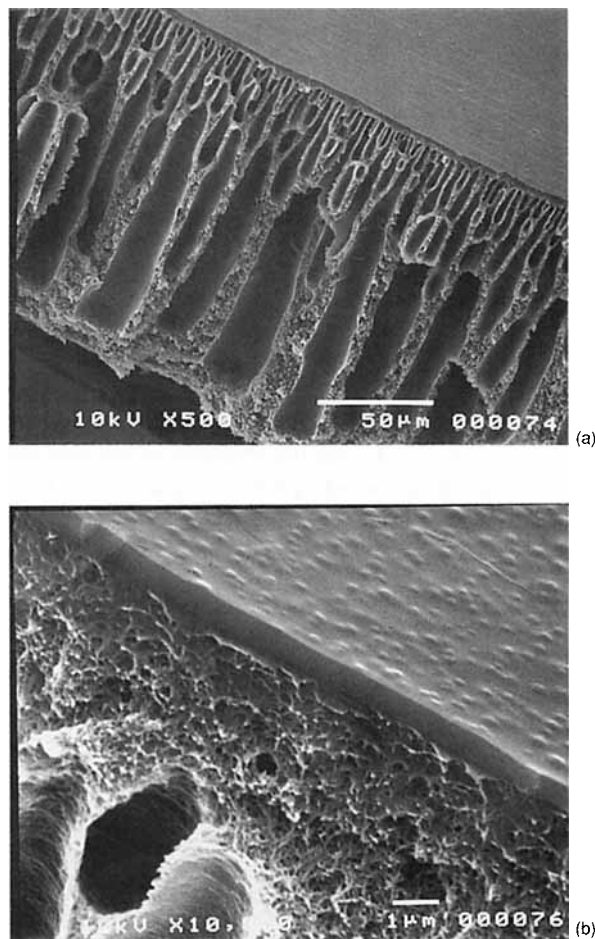


Figure 10 SEM of spin-coated membrane, 25 wt % PEI spin-coated with 15 wt % SR: (A) magnification $\times 500$; (B) magnification $\times 10,000$.

For both dip- and spin-coating techniques, uniform thin-coating was difficult to obtain when the coating solutions contained a low concentration of SR. This lack of uniformity led to poor separation. To obtain a more uniform coating, higher concentrations of SR solutions were used. The coating thicknesses obtained from the dip-coating technique were generally much thicker than those obtained when the spin-coating technique was used.

CONCLUSIONS

From the above experimental results for the pervaporation of acetic-acid/water mixtures, and for the evaluation of spin- and dip-coating techniques, the following conclusions can be drawn:

1. Polyetherimide (PEI) membranes are water-selective.
2. The water-selectivity of PEI membranes is increased when spin- or dip-coated with a polydimethylsiloxane (SR) solution.
3. PEI membranes coated with SR solutions of increasing concentration have increased water-selectivity, although decreased permeate flux. For pervaporation, a SR coating concentration of 2 wt % (in hexane), spin-coated onto a 25 wt % PEI membrane, was determined as the smallest effective coating concentration. Coating concentrations below this value did not effectively coat the membrane surface.
4. From a comparison of spin-coating thickness estimates, the coating solution penetrates the membrane pores before coating the surface of the membrane.
5. The spin-coating technique provides a thinner, more uniform coating than the dip-coating technique.

REFERENCES

1. R. Y. M. Huang, Ed., *Pervaporation Membrane Separation Processes*, Elsevier, New York, 1991.
2. H. E. A. Bruschke, in R. Bakish, Ed., *Proc. of Fourth Int. Conf. on Pervaporation Processes in the Chem. Ind.*, Bakish Materials Corp., Englewood, NJ, 1989, pp. 1-12.
3. K. W. Böddeker, G. Bengston, and E. Bode, *J. Membrane Sci.*, **53**, 143 (1990).
4. S. Deng, S. Sourirajan, and T. Matsuura, in R. Bakish, Ed., *Proc. of Fourth Int. Conf. on Pervaporation Processes in the Chem. Ind.*, Bakish Materials Corp., Englewood, NJ, 1989, pp. 84-92.
5. J. Bai, A. E. Fouda, and T. Matsuura, et al., *J. Appl. Polym. Sci.*, **48**, 999-1008 (1993).
6. K. Nakamae, T. Miyata, and T. Matsumoto, *J. Membrane Sci.*, **69**, 121 (1992).
7. Y. Chen, T. Miyano, and A. Fouda, et al., *J. Membrane Sci.*, **48**, 203 (1990).
8. M. Ohring, Ed., *The Materials Science of Thin Films*, Harcourt Brace Jovanovich, San Diego, CA, 1992.
9. J. L. Vossen, Ed., *Thin Film Processes II*, Harcourt Brace Jovanovich, San Diego, 1991.
10. R. P. Spiers, C. V. Subbaraman, and W. L. Wilkinson, *Chem. Eng. Sci.*, **30**, 379-395 (1975).
11. W. A. Levinson, A. Arnold, and O. Dehdogins, *Polym. Eng. Sci.*, **33**, 980 (1993).
12. J. D. Le Roux and D. R. Paul, *J. Membr. Sci.*, **74**, 233-252 (1992).
13. D. E. Bornside, C. W. Macosko, and L. E. Scriven, *J. Imaging Technol.*, **13**, 122 (1987).
14. D. Meyerhofer, *J. Appl. Phys.*, **49**, 3993 (1978).
15. A. G. Emslie, F. T. Bonner, and L. G. Peck, *J. Appl. Phys.*, **29**, 858 (1959).
16. L. E. Scriven, in *Better Ceramics Through Chemistry III*, C. J. Brinker, D. E. Clark, and D. R. Ulrich, Eds., MRS, Pittsburgh, 1988, p. 717.
17. S. Sourirajan and T. Matsuura, Eds., *Reverse Osmosis/Ultrafiltration Process Principles*, National Research Council of Canada, Ottawa, 1985.
18. J. M. S. Henis and M. K. Tripodi, U. S. patent 4,230,463 (1980).
19. S. Henis and M. Tripodi, *Sep. Sci. Technol.*, **15**, 1059 (1980).
20. J. M. S. Henis and M. K. Tripodi, *J. Membrane Sci.*, **8**, 233 (1981).
21. A. Fouda, Y. Chen, and J. Bai, et al., *J. Membrane Sci.*, **64**, 263-271 (1991).
22. General Electric Permeable Membranes, issued as General Electric Bulletin GEA-8685B-3-82.

Received December 17, 1993

Accepted April 16, 1994