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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Mu-Hoe Yang[a]; Tzong-Jeng Chu[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL CHENG KUNG UNIVERSITY, TAINAN, TAIWAN, REPUBLIC OF CHINA

To cite this Article Yang, Mu-Hoe and Chu, Tzong-Jeng(1993) 'The Effect of Skin Layer Composition and Operating Parameters on the Performance of Sulfonated Polysulfone-Poly(Vinyl Alcohol) Composite Reverse Osmosis Membrane', Separation Science and Technology, 28: 6, 1315 — 1326

To link to this Article: DOI: 10.1080/01496399308018039

URL: http://dx.doi.org/10.1080/01496399308018039

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SEPARATION SCIENCE AND TECHNOLOGY, 28(6), pp. 1315–1326, 1993

The Effect of Skin Layer Composition and Operating Parameters on the Performance of Sulfonated Polysulfone–Poly(Vinyl Alcohol) Composite Reverse Osmosis Membrane

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MU-HOE YANG* and TZONG-JENG CHU
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL CHENG KUNG UNIVERSITY
TAINAN, TAIWAN 70101, REPUBLIC OF CHINA

ABSTRACT

A composite membrane for reverse osmosis was prepared from sulfonated polysulfone and poly(vinyl alcohol). The effects of overall polymer solution concentration, composition of casting solution, and heat-curing periods on the reverse osmosis performance of the resulting membrane have been examined. The composite membrane was formed by casting the polymer solution as an ultrathin film on a microporous polysulfone supporter, evaporating the solvent, and heat curing at 120°C for a proper period. The influence of different operating parameters on the performance of the resulting membrane was examined. The results showed that the flux of water increased and salt rejection increased with an increase in the ratio of sulfonated polysulfone to poly(vinyl alcohol) (SPSf/PVA). The flux of water is proportional to the operating pressure of the formed membrane with an SPSf/PVA ratio of 3/3–4/2. The flux of water was found to be a highly nonlinear function of the operating pressure of the formed membrane with an SPSf/PVA ratio of 2/4–0/6.

INTRODUCTION

Membrane separation processes are playing an increasing role in such applications as water desalination, industrial and municipal waste treatment, and bioengineering in Taiwan. Some commercial products have been widely used for such reverse osmosis separations as cellulose acetate and aromatic polyamide. However, that membrane is limited in its resistance

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*To whom correspondence should be addressed.

to chemicals, oxidation, and bacteria. Therefore, it would be interesting to develop new membranes from other synthetic polymers.

Because of its chemical, thermal stability, and high water permeability (1–3), poly(vinyl alcohol) is an attractive material for producing membranes. However, since it is highly hydrophilic, its unmodified membranes are highly permeable to water and salt, so they need to be improved. Some studies have been reported in the literature (4–6). In most earlier studies, the modified PVA membranes were prepared by crosslinking with aldehydes and dicarboxylic acids or by heat treatment. The recent preparation of new PVA membranes has focused on blending with sulfonated polymers (7). Among sulfonated polymers, sulfonated polysulfone has been reported to be useful in desalination applications (8–10). Polysulfone is a high-performance, tough, high-temperature-resistant thermoplastic resin (11); however, its somewhat hydrophobic nature precludes its use in membrane applications. As such, it is an excellent candidate for chemical modification by sulfonation.

In this study, thin film composite membranes were prepared from sulfonated polysulfone and poly(vinyl alcohol) (SPSf-PVA) with polysulfone (PSf) as the substrate. The preparation and performance of SPSf-PVA composite membranes under various conditions were examined to determine the performance of SPSf-PVA composite reverse osmosis membranes.

EXPERIMENTAL

Reagents

The poly(vinyl alcohol) (PVA) used in these experiments was Elvanol grade 85–82 (DuPont de Nemours & Co., Wilmington, Delaware) with a number-average molecular weight ($\overline{M}_n$) of 52,800 and a polydispersity index ($\overline{M}_w/\overline{M}_n$) of 2.14 (12). The polysulfone was UDEL P-1700 with an $\overline{M}_n$ of 20,000–24,000 and a weight-average molecular weight ($\overline{M}_w$) of 35,000 (13). Isopropanol and other chemicals were reagent grade and used without further purification.

Preparation of MF Polysulfone Membrane

To prepare the microporous polysulfone substrate, a 15 wt% solution of polysulfone in dimethylacetamide was drawn out on a flat glass plate by using a doctor knife to obtain a 200-μm thick uniform film. The plate was immediately immersed in a water bath at 25°C in one smooth motion. Within 30 seconds, a white microporous sheet formed and was lifted away from the glass surface. After 5 minutes, the polysulfone support was removed, rinsed with fresh water, then stored in deionized water until used.

The top surface (air side) was used as the support surface for membrane formation. The mean flow pore size was 0.15 μm as measured by a bubble point tester (ASTM F316-80).

Sulfonation of Polysulfone

Sulfonated polysulfone was prepared by sulfonation of polysulfone with chlorosulfonic acid ($HClSO_3$) in 1,2-dichloroethane at −20°C and purified. The sulfonic acid content was 1.2 meq/g as determined by the method of Fisher and Kunin (14).

Preparation of Thin Film Composite Membrane

The composite membrane was formed by casting (casting thickness, 0.05 mm) the polymer solution into a thin film on a microporous polysulfone supporter, evaporating the solvent at 30°C and 40% relative humidity for 2 hours, and then heat curing at 120°C for a proper period. A mixture of water and isopropanol (1/1, vol%) was found to be a proper solvent for casting a membrane on the supporter. The resulting composite membrane had a dense homogeneous structure due to the membrane formed by complete evaporation of the solvent and heat curing at high temperature. Before membrane performance was measured, the membrane was preconditioned with 1 N NaOH, 1 N HCl, and 1 N NaCl, and converted into the Na form.

Permeation Experimental

The testing cell is shown in Fig. 1. The cell is 4 cm in diameter, and the gap for flow between the upper and lower plates is 2 cm. The fluid was agitated by a magnetic stirrer operating at under 1200 rpm at a given temperature. It was run through two cells connected in series and operating at different pressures and temperatures.

The entire testing cells were immersed in a water bath at a constant temperature. The desired pressure was applied to the upstream side, and enough time was allowed for a steady permeation rate to be established. A sample was collected every hour, and it was converted to volume flux, J_w, in $L/m^2 \cdot h$. In each experiment the concentrations of sodium chloride in the feed solution and in the permeate were obtained from conductivity measurements. Percent rejection was calculated according to the following relation:

$$\% \text{ rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

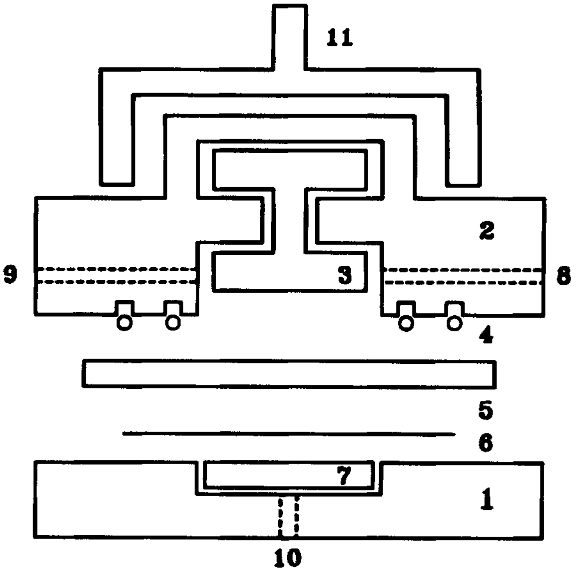

FIG. 1 A scheme of a high-pressure testing cell. 1, Upper cell; 2, lower cell; 3, stirrer; 4, O-ring; 5, membrane; 6, filter paper; 7, porous steel plate; 8, feed in; 9, concentrate out; 10, permeate out; 11, magnetic stirrer shaft.

where C_p is solute concentration in the permeate solution and C_f is solute concentration in the feed solution.

RESULTS AND DISCUSSION

Fabrication Conditions of the Membrane

The effect of the heat-curing period on membrane performance was examined by varying the heat-curing period for a polymer with an SPSf/PVA ratio of 4/2 and an overall polymer concentration of 6.0 wt% at 120°C. The results obtained are shown in Fig. 2. When the heat-curing period was varied for 1–4 hours, an increase in the heat-curing period leads to a water flux decrease and a salt rejection increase of the membrane.

The effect of overall polymer concentration in the casting solution on membrane performance was examined by varying the casting solution concentration of a membrane for a polymer with an SPSf/PVA ratio of 1/1 that was heat cured at 120°C for 4 hours. The results obtained are shown in Fig. 3. When the overall polymer concentration in the casting solution was varied in the 2.0–6.0 wt% range, the salt rejection increased and the water flux decreased with an increase in polymer concentration. However, when

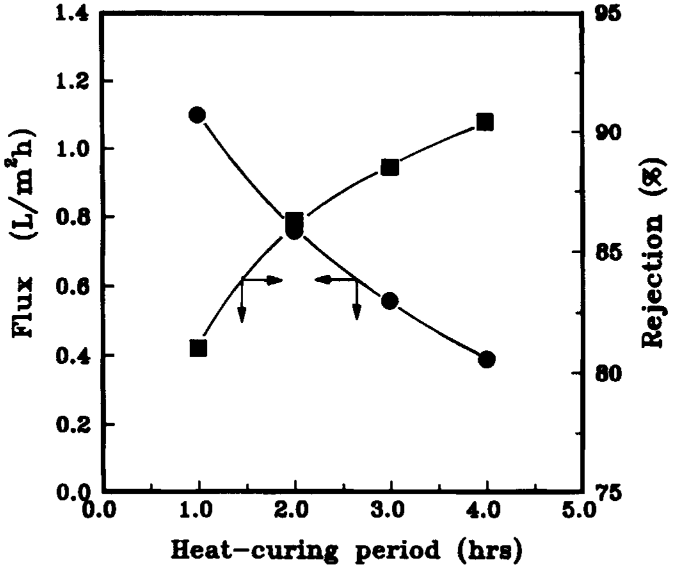

FIG. 2 Effect of heat-curing period on the membrane performance. Casting solution, 6.0 wt% (SPSf/PVA ratio of 4/2); heat-curing temperature, 120°C; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

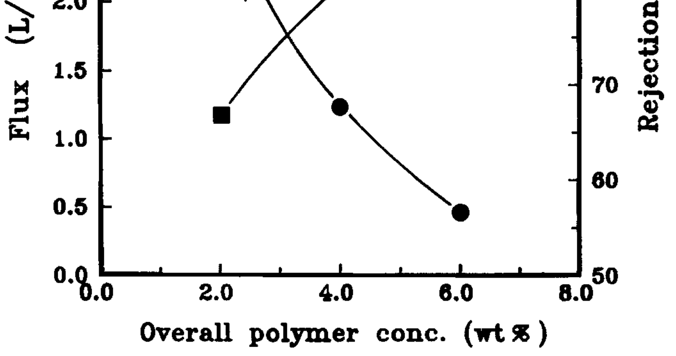

FIG. 3 Effect of overall polymer concentration in casting solution on the membrane performance. SPSf/PVA ratio of 1/1; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

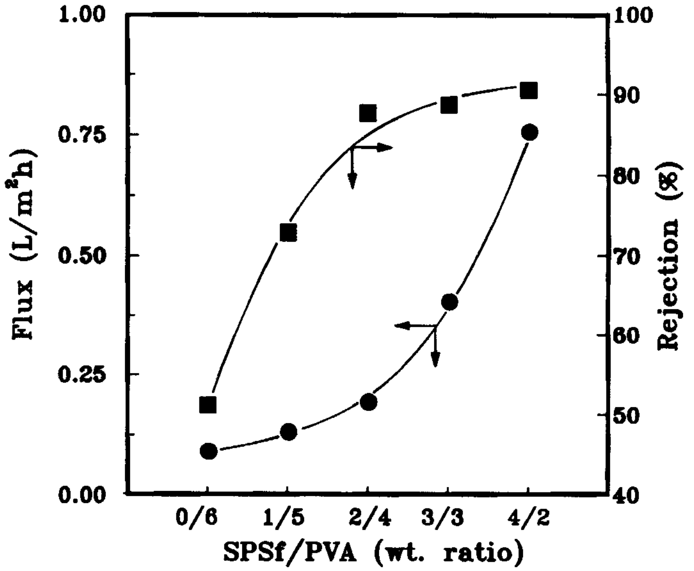

FIG. 4 Effect of weight ratio of SPSf/PVA in casting solution on the membrane performance. Overall polymer concentration, 6.0 wt%; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

the overall polymer concentration was less than 2.0 wt% or more than 6.0 wt%, the viscosity of the polymer solution was not desirable for membrane casting.

The effect of the ratio of SPSf to PVA on membrane performance was examined by varying the ratio of SPSf to PVA at an overall polymer concentration of 6.0 wt% and heat curing at 120°C for 4 hours. The results obtained, shown in Fig. 4, show that water flux and salt rejection increased with an increase in the ratio of SPSf to PVA. The sulfonated polysulfone membrane has larger water flux and salt rejection. However, when the ratio of SPSf to PVA is more than 4/2, the fragile nature of the membrane is not desirable for membrane testing.

Membrane Performance for Various Fabrication Conditions

The effects of applied pressure on the performance of the resultant membrane are shown in Figs. 5, 6, and 7. Membranes were formed by casting from polymer solution concentrations of 2.0–6.0 wt% or an SPSf/PVA ratio of 0/6–4/2 on a microporous PSf supporter, evaporating the solvent at 30°C and 40% relative humidity for 4 hours, and then heat curing at 120°C for 4 hours. The experiment was carried out at an applied pressure under 1.0–9.0 MPa.

As shown in Fig. 5, water flux and salt rejection increased with an increase in applied pressure. Membranes were formed by casting the overall polymer solution concentration at 2.0–6.0 wt% (SPSf/PVA ratio of 1:1). The water flux is proportional to the applied pressure. However, salt rejection was found to be a highly nonlinear function of the applied pressure.

As shown in Figs. 6 and 7, water flux increased and salt rejection increased with an increase in operating pressure. Membranes were formed by casting at a polymer composition SPSf/PVA ratio of 0/6–4/2 (overall polymer concentration, 6.0 wt%). A straight line exists between water flux and operating pressure for membranes formed at a SPSf/PVA ratio of 3/3–4/2. However, the relationship between water flux and operating pressure is nonlinear for membranes formed at an SPSf/PVA ratio of 0/6–2/4. In the case of polymer composition with an SPSf/PVA ratio of 0/6–2/4, there is a slight compaction under the influence of applied pressure, the membrane has a larger water content, and it has a tendency to swell.

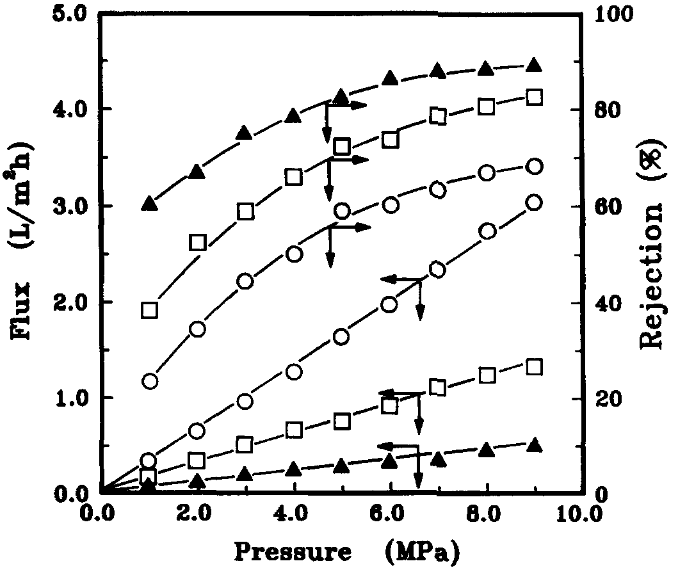

FIG. 5 Effect of applied pressure on the membrane performance. Casting: (○) 2.0 wt%, (□) 4.0 wt%, (▲) 6.0 wt%; SPSf/PVA ratio, 1/1; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

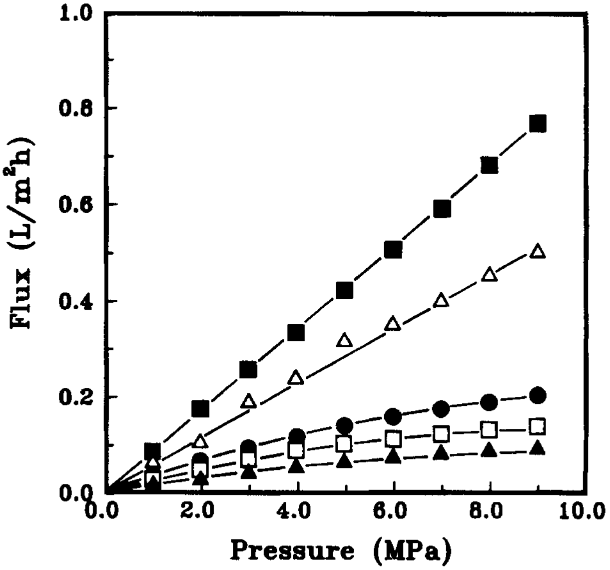

FIG. 6 Effect of applied pressure on the membrane performance. SPSf/PVA ratio: (■) 4/2, (△) 3/3, (●) 2/4, (□) 1/5, (▲) 0/6; overall polymer concentration; 6.0 wt%; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

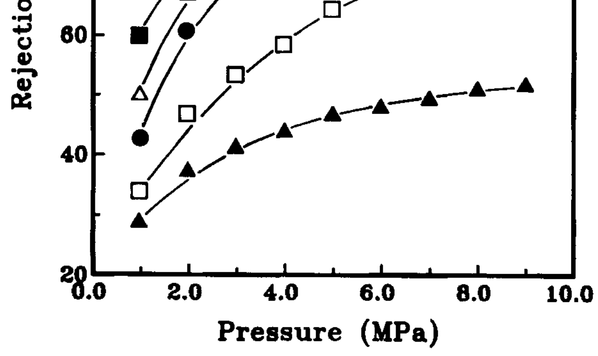

FIG. 7 Effect of applied pressure on the membrane performance. SPSf/PVA ratio: (■) 4/2, (△) 3/3, (●) 2/4, (□) 1/5, (▲) 0/6; overall polymer concentration, 6.0 wt%; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

Moreover, salt rejection was found to be a highly nonlinear function of applied pressure for all membranes of polymer composition with an SPSf/PVA ratio of 0/6–4/2.

The effects of temperature on the performance of the membranes are shown in Figs. 8, 9, and 10. The experiment was carried out at 20–50°C. As shown in Fig. 8, salt rejection sight decreased slightly and water flux increased with an increase in temperature. The membranes were formed by casting the overall polymer concentration at 2.0–6.0 wt% (SPSf/PVA ratio of 1:1).

As shown in Figs. 9 and 10, water flux increased and salt rejection decreased with an increase in temperature. The membranes were formed by casting at a polymer composition SPSf/PVA ratio of 0/6–4/2 (overall polymer concentration, 6.0 wt%). Moreover, salt rejection decreased slightly with an increase in temperature for membranes formed at an SPSf/PVA ratio of 3/3–4/2. However, salt rejection strongly decreased with temperature for membranes formed at an SPSf/PVA ratio of 0/6–2/4. These results suggest that the viscosity of the water will decrease with increasing temperature, and thus the water flux through the membrane will increase (15). Especially at a lower SPSf/PVA ratio, the membranes will swell in

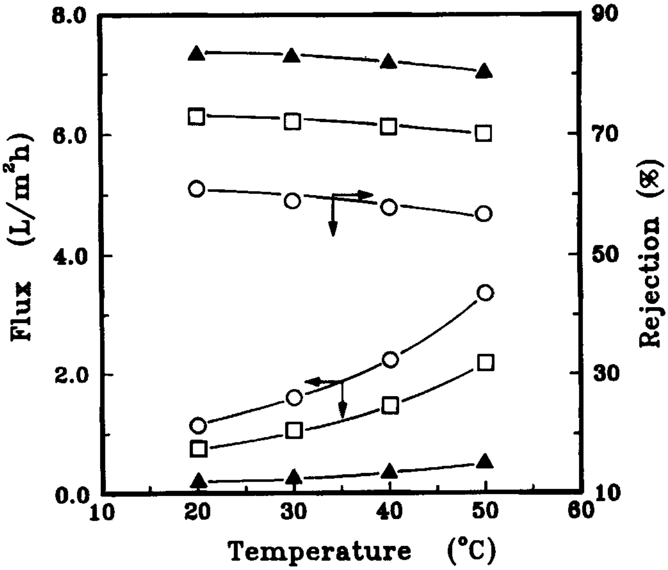

FIG. 8 Effect of temperature on the membrane performance. Casting: (○) 2.0 wt%, (□) 4.0 wt%, (▲) 6.0 wt%; SPSf/PVA ratio, 1/1; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

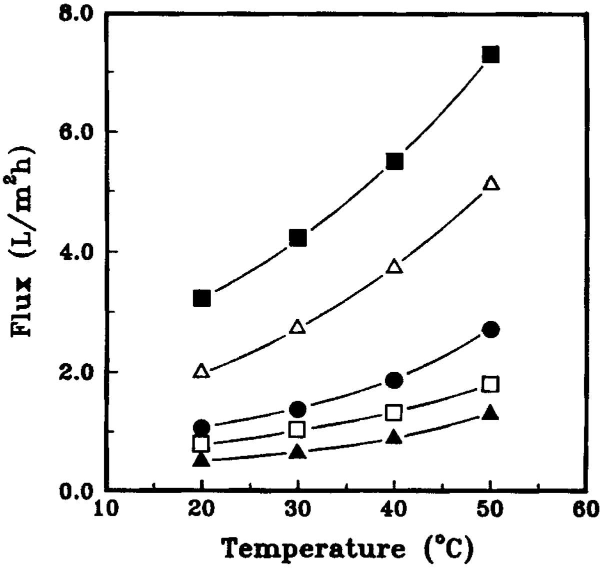

FIG. 9 Effect of temperature on the membrane performance. SPSf/PVA ratio: (■) 4/2, (△) 3/3, (●) 2/4, (□) 1/5, (▲) 0/6; overall polymer concentration, 6.0 wt%; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

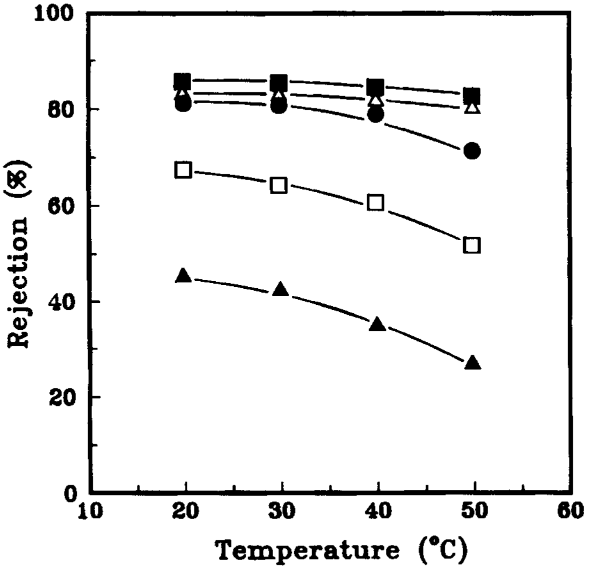

FIG. 10 Effect of temperature on the membrane performance. SPSf/PVA ratio: (■) 4/2, (△) 3/3, (●) 2/4, (□) 1/5, (▲) 0/6; overall polymer concentration, 6.0 wt%; heat-curing temperature, 120°C for 4 hours; applied pressure, 80 kg/cm^2; feed solution, 0.35% NaCl aqueous solution.

water, and salt rejection will significantly decrease with an increase in temperature.

CONCLUSIONS

A composite membrane for reverse osmosis was prepared from sulfonated polysulfone and poly(vinyl alcohol) with polysulfone as the substrate. The effects of fabrication conditions on the performance of an SPSf-PVA composite membrane were examined. It was found that the optimum composition of a casting solution was as follows: percent of sulfonated polysulfone/poly(vinyl alcohol)/solvent was 4/2/94. A mixture of water and isopropanol (1/1, vol%) was used as the solvent.

The effects of operating conditions on the performance of the resulting membrane were examined. The membrane was formed by casting from solution and heat curing at 120°C for 4 hours to give an acceptable salt rejection for reverse osmosis, viz., a water flux of 0.086–0.68 $L/m^2 \cdot h$ at a salt rejection of 50.9–90.4% under an applied pressure of 8.0 MPa with a 3500 ppm NaCl aqueous solution. The results showed that the flux of water increased and the salt rejection increased with an increase in the ratio of SPSf to PVA. The results indicated that the larger the ratio of SPSf to PVA, the better the applicability as a reverse osmosis membrane. The water flux is proportional to the operating pressure of membranes formed at an SPSf/PVA ratio of 3/3–4/2. The flux of water was found to be a highly nonlinear function of the operating pressure of membranes formed at an SPSf/PVA ratio of 2/4–0/6. Salt rejection was found to be a highly nonlinear function of the operating pressure for all the resulting membranes.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support of this study by the National Science Council of the Republic of China. The authors' extend special thanks to Dr. J. H. Wang and Dr. J. F. Kuo for their helpful discussions and creative criticism.

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Received by editor May 4, 1992