

An Interpolymer Anionic Composite Reverse Osmosis Membrane Derived from Poly(vinyl Alcohol) and Poly(styrene Sulfonic Acid)

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Synopsis

An interpolymer anionic composite membrane for reverse osmosis was prepared from poly(vinyl alcohol) and poly(styrene sulfonic acid). The effects of composition of a casting solution, heat-curing periods, and casting thickness on the reverse osmosis performance of resulted membranes have been examined. A mixture of water and ethyl alcohol (12/7, wt %) was found to be a proper solvent for casting an interpolymer membrane on the supporter. The composite membrane was formed by casting the polymer solution in ultrathin film on a microporous polypropylene supporter, evaporating the solvent, and heat-curing at 120°C for a proper period. The optimum composition of a casting solution was as follows: wt % of poly(vinyl alcohol)/poly(styrene sulfonic acid)/solvent was 3/2/95. The membrane heat-cured at 120°C for 2 h has a good performance for reverse osmosis, viz., water flux of 9.1–28.4 L/m²·h at salt rejection level of 88.1–93.4% under applied pressure of 80 kg/cm² with 0.5% NaCl aqueous solution. The formation mechanism of a water-insoluble membrane was discussed.

INTRODUCTION

Cellulose acetate or aromatic polyamide membranes have been widely used for reverse osmosis separation. However, these membranes have exhibited flux declines, and are limited in resistance ability for chemicals, oxidation, and bacteria.

Recently, the preparation of new type membranes from other synthetic polymers have been investigated extensively.¹ In these studies, much interest is focused on charged membranes. It may be expected that solute separation by charged membranes is different from one by noncharged neutral membranes, i.e., cellulose acetate and aromatic polyamide, by the ion-exclusion effect of fixed charged groups in membranes.

Also charged membranes are prepared from excellent polymeric materials in physicochemical resistance. It has been reported that anionic charged membranes were prepared from sulfonated polyphenylene oxide,² sulfonated polysulfone,^{3,4} poly(styrene sulfonic acid),^{5,6} etc.

This paper deals with the preparation and performance of an interpolymer anionic composite membrane. An interpolymer membrane was prepared from poly(vinyl alcohol) as a membrane matrix and linear poly(styrene sulfonic acid) as an ionic component.

EXPERIMENTAL

Poly(vinyl alcohol) PVA-H (PVA) (average degree of polymerization, $\overline{P}_n = 1700$) supplied by Kuraray Co. Ltd., was used. Poly(styrene sulfonic acid) (PSSA) was prepared by sulfonation of polystyrene with concn H_2SO_4 in CCl_4 and purified. The sulfonic acid content and molecular weight of the PSSA were 4.12 meq/g and 123,000, respectively. Ethyl alcohol (EtOH) and others were used as reagent grade chemicals without further purification. Microporous filter Duragard 2500 (average pore radius 1000 Å) supplied by Polyplastics Co., Ltd., was used as a membrane supporter.

Membrane materials were PVA as a membrane matrix and linear water-soluble PSSA as a polyelectrolyte. A mixture of water and EtOH (12/7, wt %) was selected as a casting solvent. This mixture was able to dissolve homogeneously both polymers. Also, the value of surface tension of the casting solution was 35.7 dyn/cm at 30°C and almost the same with one of the polypropylene supporter (34 dyn/cm).⁷ This composition of casting solution was very desirable for casting a polymer solution uniformly on the supporter. Another composition was not proper for the following two factors: surface tension and solubility for both polymers.

The composite membrane was formed by casting the polymer solution into a thin film on a polypropylene microporous supporter (Duragard 2500), evaporating the solvent at 30°C for 1 h, and then heat-curing at 120°C for a proper period. The resultant interpolymer membrane had a dense homogeneous structure due to the membrane formation by evaporating the solvent completely and heat-curing at higher temperature.

Before measurement of the membrane performance, a membrane was pre-conditioned with 1 N NaOH, 1 N HCl, and 1 N NaCl, and converted into Na form.

The apparatus and experimental details were the same as the one in a previous paper⁴.

RESULTS AND DISCUSSIONS

Fabrication Conditions of the Membrane

The effect of the polymer concentration in the casting solution on the membrane performance was examined with variation in the casting solution concentration and membrane casting thickness on the membrane with polymer composition of PVA/PSSA ratio of 3/2, and heat-cured at 120°C for 2 hrs. The results obtained are shown in Figure 1.

When polymer concentration in the casting solution was varied at the range of 2.5–7.5 wt %, salt rejection increased, and water flux decreased with increase in the polymer concentration. Variation of salt rejection and water flux were less at higher than 5 wt % polymer concentration.

Membrane casting was carried out in a spacer thickness of 0.03 mm and 0.10 mm. The former had higher water flux and lower salt rejection than the latter. However, the variation of the membrane performance showed a similar trend. When the polymer concentration was less than 2.5 wt % or more than 7.5 wt %, the viscosity of polymer solution was not desirable for membrane casting.

The effect of the ratio of PVA to PSSA on the membrane performance was

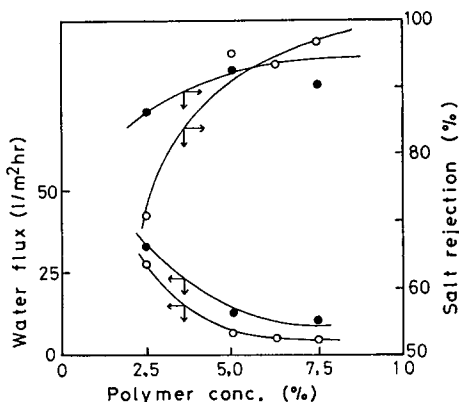


Fig. 1. Effect of polymer concentration in casting solution on the membrane performance. Casting thickness (mm): (●) 0.03; (○) 0.10; PVA/PSSA ratio of 3/2; heat-curing, 120°C for 2 h; applied pressure, 80 kg/cm².

examined with variation in the ratio of PVA to PSSA. The results obtained are shown in Figure 2. In this case, the other conditions for membrane formation were kept the same.

Water flux decreased with increase in the ratio of PVA to PSSA. On the other hand, salt rejection was maximum in polymer composition of PVA/PSSA ratio of 3/2.

In the case of polymer composition of PVA/PSSA ratio of 1/1, the membrane had higher water flux and lower salt rejection more than any other membrane. The resultant membrane had a larger water content and tended to swell.

Conversely, in the case of polymer composition of PVA/PSSA ratio of 2/1, an ion exchange capacity of the resultant membrane was smaller with lower PSSA content in the membrane. Also, the interstitial ionic concentration in the membrane is low.^{6,8} Due to these facts, the membrane had lower salt rejection. Further, the network structure of the membrane is getting more dense by heat-curing, and water content in the membrane is reduced. The resultant membrane had poor water flux.

The effect of membrane casting thickness on the membrane performance was

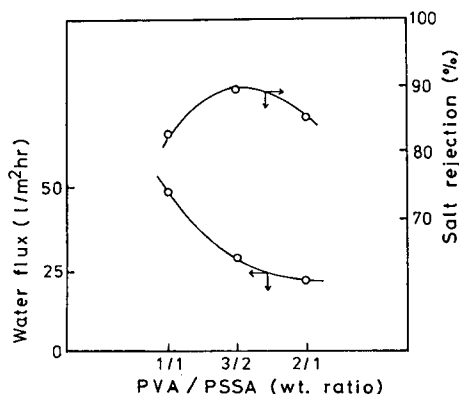


Fig. 2. Effect of weight ratio of PVA and PSSA in casting solution on the membrane performance. Polymer concentration, 5 wt %; casting thickness, 0.03 mm; heat-curing, 120°C for 2 h; applied pressure, 80 kg/cm².

TABLE I
Effect of Membrane Casting Thickness on Membrane Performance^a

PVA/PSSA ratio	Casting thickness (mm)	Concentration of polymer solution (wt %)							
		7.5		6.25		5.0		2.5	
		Flux (L/m ² ·h)	R _s (%)	Flux (L/m ² ·h)	R _s (%)	Flux (L/m ² ·h)	R _s (%)	Flux (L/m ² ·h)	R _s (%)
2/1	0.10	—	—	3.78	89.8	12.4	92.3	32.4	85.7
2/1	0.03	5.07	97.5	6.62	95.2	91.8	64.2	96.3	58.0
3/2	0.10	4.89	96.4	5.66	95.0	6.58	94.9	22.3	89.2
3/2	0.03	11.5	92.5	22.8	89.0	17.7	92.0	36.6	80.9

^a Heat-curing, 120°C for 2 h; applied pressure, 80 kg/cm²; feed solution, 0.5% NaCl aqueous solution.

examined with variation in casting thickness and solution concentration. Other conditions were kept the same. The results obtained are shown in Table I.

In the case of polymer composition of PVA/PSSA ratio of 3/2, the resultant membrane of casting thickness at 0.03 mm had higher water flux and lower salt rejection than the one of the membrane of casting thickness at 0.10 mm.

The effect of heat-curing period on the membrane performance was examined at 120°C. The results obtained are shown in Figures 3 and 4. In all cases, an increase in heat-curing period gave rise to water flux decrease and salt rejection increase of the membrane. The membrane performance was changed significantly with heat-curing period up to 2 h. However, variation of the membrane performance was less at longer than 2 h.

Membrane Performance for Various Fabrication Conditions

The relationship between water flux and salt rejection of formed membranes (practical membranes) at various fabrication conditions are shown in Figures 5 and 6. These membranes have water flux of 3–150 L/m²·h and salt rejection of 99–45% under applied pressure of 80 kg/cm² with 0.5% NaCl aqueous solution, and salt rejection is proportional to water flux over the wide range.

The effects of applied pressure on the performance of the resultant membrane

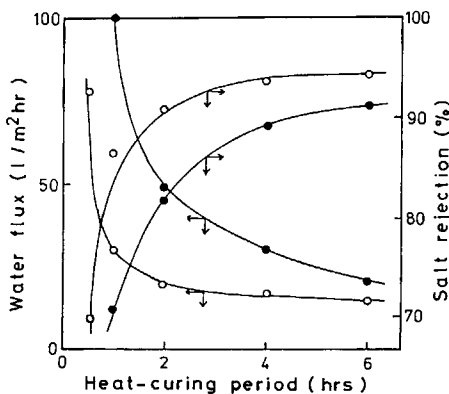


Fig. 3. Effect of heat-curing period on the membrane performance. Casting solution: (●) 5 wt % (PVA/PSSA ratio of 1/1); (○) 5 wt % (PVA/PSSA ratio of 3/2); casting thickness, 0.03 mm; heat-curing temperature, 120°C; applied pressure, 80 kg/cm².

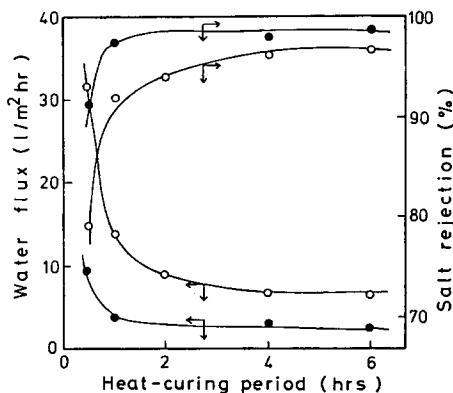


Fig. 4. Effect of heat-curing period on the membrane performance. Casting solution, 6.25 wt % (PVA/PSSA ratio of 2/1); casting thickness (mm): (O) 0.03; (●) 0.10; heat-curing temperature, 120°C; applied pressure, 80 kg/cm².

are shown in Figure 7. Membranes were formed by casting the polymer solution concentration at 2.5 or 5.0 wt % (PVA/PSSA ratio of 3/2), on a polypropylene microporous supporter, evaporating the solvent at 30°C for 1 h, and then heat-

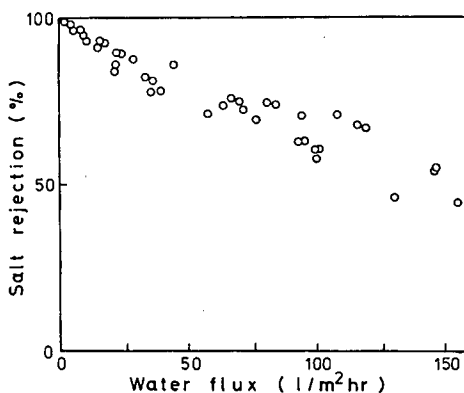


Fig. 5. Water flux and salt rejection of the composite membranes. Polymer concentration, 5 wt %; PVA/PSSA ratio of 3/2; heat-curing, 120°C; applied pressure, 80 kg/cm².

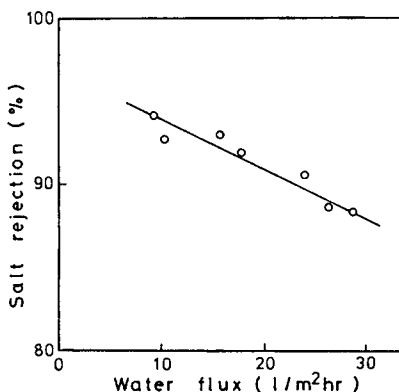


Fig. 6. Water flux and salt rejection of the composite membranes. Polymer concentration, 5 wt %; PVA/PSSA ratio of 3/2; heat-curing, 120°C; applied pressure, 80 kg/cm².

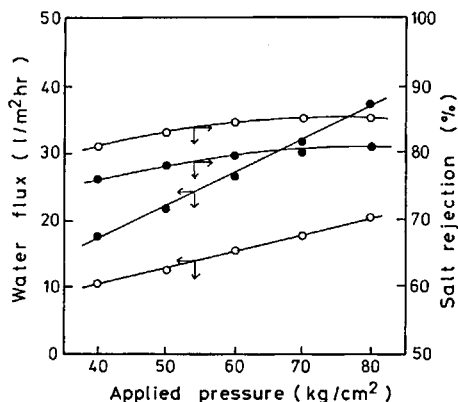


Fig. 7. Effect of applied pressure on the membrane performance. Casting solution: (●) 2.5 wt % (PVA/PSSA ratio of 3/2); (○) 5.0 wt % (PVA/PSSA ratio of 3/2); heat-curing, 120°C for 2 h.

curing at 120°C for 2 h. The experiment was carried out at applied pressure under 40–80 kg/cm².

As shown in Figure 7, water flux and salt rejection increased with increase in applied pressure. Water flux is proportional to applied pressure. The membrane would have undergone a slight compaction under the influence of applied pressure, and subsequently the interstitial ionic concentration in the membrane increases. Therefore, salt rejection increases with applied pressure.

Formation Mechanism of Water-Insoluble Membranes

The membrane was prepared by casting a 5 wt % polymer solution (PVA/PSSA ratio of 3/2) in 0.2 mm thickness on a polyethylene film and then dried at room temperature or heat-cured at 120°C for up to 6.5 h. Infrared spectra of films are shown in Figure 8.

The infrared spectrum of a non-heat-cured membrane is identical to that of mixture of PVA and PSSA. On the other hand, new absorption bands appeared

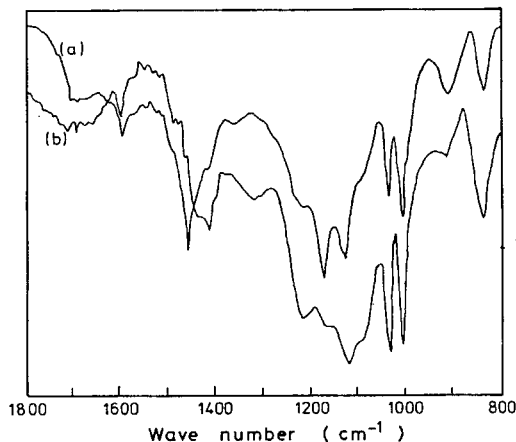


Fig. 8. Infrared spectra of composite membranes. (a) heat-cured membrane, 120°C for 6.5 h; (b) non-heat-cured membrane.

at 1170 cm^{-1} and 1460 cm^{-1} in the infrared spectrum of a heat-cured membrane. These two absorption bands become stronger with increase in heat-curing period, and the absorption band attributable to hydroxyl groups is reduced.

These results suggest that the $\text{R}-\text{O}-\text{SO}_2-\text{R}$ bond is formed by dehydration between two polymers and also the intermolecular dehydration of PVA would occur in the presence of PSSA. These reactions do not occur between PVA and Na salt of PSSA by heat-curing.⁸ The membrane may be crosslinked by these mechanisms and thus become water-insoluble.

CONCLUSIONS

An interpolymer anionic composite membrane for reverse osmosis was prepared from poly(vinyl alcohol) as a membrane matrix and poly(styrene sulfonic acid) as a water-soluble polyelectrolyte. The optimum composition of a casting solution was follows: % of poly(vinyl alcohol)/poly(styrene sulfonic acid)/solvent was 3/2/95. A mixture of water and ethyl alcohol (12/7, wt %) was used as a solvent.

The membrane was formed by casting the solution and heat-curing at 120°C for 2 h to give a good performance for reverse osmosis, viz., water flux of 9.1–28.4 $\text{L}/\text{m}^2\cdot\text{h}$ at salt rejection of 88.1–93.4% under applied pressure of $80\text{ kg}/\text{cm}^2$ with 0.5% NaCl aqueous solution.

An interpolymer membrane is crosslinked and water-insoluble by the formation of an $\text{R}-\text{O}-\text{SO}_2-\text{R}$ bond by dehydration between both polymers, and intermolecular dehydration of PVA in the presence of PSSA under heat-curing.

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