

Formation of Integrally Skinned Asymmetric Polyetherimide Nanofiltration Membranes by Phase Inversion Process

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ABSTRACT: Integrally skinned asymmetric polyetherimide (PEI) membranes were prepared by the phase inversion process from casting solution containing dimethylformamide (DMF) as a solvent and 1,4-dioxane as a cosolvent. Deionized water was used as a coagulation medium in preparing asymmetric membranes. The effect of 1,4-dioxane was investigated by measuring casting solution properties, permeation properties, and membrane structures. Various effects of polymer concentration, evaporation time, and coagulation bath temperature were also studied. Low miscibility of 1,4-dioxane with coagulant (water) resulted in reducing membrane pore size. The molecular weight cutoff values of asymmetric membranes could be controlled by changing the amount of 1,4-dioxane in the casting solution. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1300–1307, 2002; DOI 10.1002/app.10452

Key words: polyetherimide; asymmetric membrane; cosolvent; 1,4-dioxane; miscibility; molecular weight cutoff

INTRODUCTION

Asymmetric membranes are generally prepared by the phase inversion method, especially the immersion precipitation process.^{1–3} In other words, a casting solution consisted of polymer and solvent mixture is immersed into a nonsolvent coagulation bath. The membrane is formed by the interchange of solvent and nonsolvent coagulant due to the diffusion. Since the asymmetric-type membranes were prepared by Loeb and Sourirajan, the development of the phase inversion technique has preceded many systematic studies on the effects of membrane formation parameters and mechanism. Surface properties of membranes can be controlled depending on the casting conditions,^{4–6} polymer solution,^{7–11} and coagulation bath compositions.¹¹ The pore-forming pro-

cesses occurring in the phase inversion process contain both the thermodynamics^{12–16} and kinetics^{17–19} of the polymer solution systems. The kinetic property mainly involves the relative diffusion rates of solvents and nonsolvents. Despite extensive research efforts, the actual pore formation mechanism is not well understood. In general, the phase inversion process involves two different phase transition (liquid–liquid phase separation and solidification). When a homogeneous polymer solution becomes thermodynamically unstable, the solution can decrease its free energy from mixing by dividing into two liquid phases of different composition (polymer-poor phase and polymer-rich phase).^{12,13} A nucleus of the polymer poor phase can form nascent pore. And a polymer-rich phase surrounds the pore. The ratio of nonsolvent inflow to solvent outflow is of the utmost importance for the top layer structure. A dense skin is formed because solvent in the casting solution desolvates rapidly into the coagulation bath. When a nonsolvent additive is

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added to a polymer–solvent solution, the interaction of the nonsolvent and solvent molecules leads to a reduction of the dissolving power of the solvent.^{20,21} And this further enhances the polymer–polymer interaction. In this case, the polymer chains may have a smaller excluded volume because of more tightly coiled conformation. The polymer aggregates are formed in the polymer solution. Thus, an initially homogeneous solution may become microscopically heterogeneous. The kinetics of phase separation during the wet coagulation process plays a major role in the control of membrane morphology.^{22–26} The accelerated rate of phase separation due to the addition of nonsolvent additive may be restricted in rearrangement of polymer aggregates, resulting in the formation of membrane with small macrovoids. If the diffusion of the solvent molecules is faster than that of the nonsolvent additive, the rapid outflow of solvent molecules will further enhance the polymer–polymer interaction before the membrane is solidified.

The purpose of this study is to prepare an asymmetric polyetherimide nanofiltration membrane with small pore size. And the effect of 1,4-dioxane additive in polyetherimide (PEI) casting solution, casting condition on membrane morphology, and performance was investigated intensively.

EXPERIMENTAL

Materials

PEI (UItem 1000, General Electric) was used as a membrane material. The polymer was dried for at

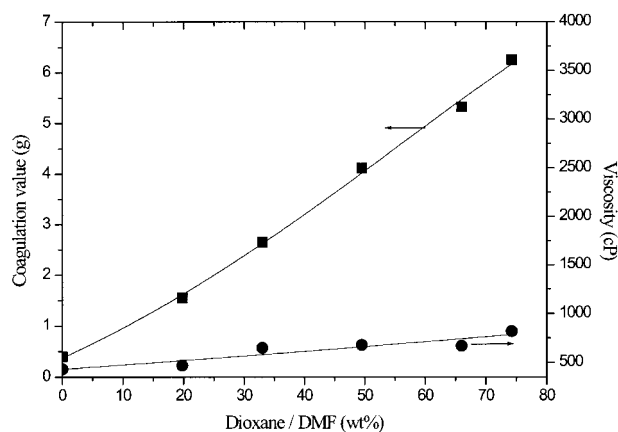


Figure 1 Effect of the ratio of 1,4-dioxane to DMF on coagulation value (1 wt % PEI concentration) and viscosity (16 wt % PEI concentration).

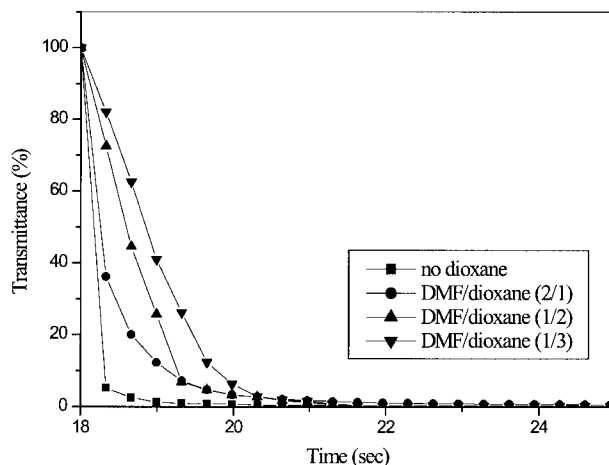


Figure 2 Effect of the ratio of 1,4-dioxane to DMF in 16wt% PEI solution on light transmission experiments. Coagulant: 25°C water.

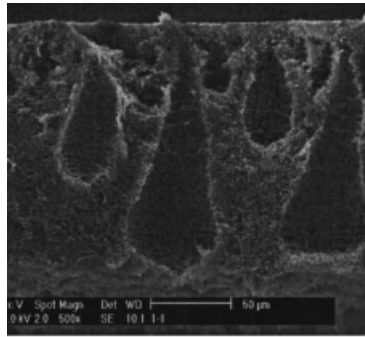
least 5 h at 100°C before being used in preparing polymer solution. Dimethylformamide [DMF; high performance liquid chromatography (HPLC) grade, Aldrich] was used as a solvent. 1,4-dioxane (HPLC grade, Aldrich) was used as a cosolvent. Deionized (DI) water was used as a coagulation media. All the chemicals were used without further purification.

Membrane Preparation

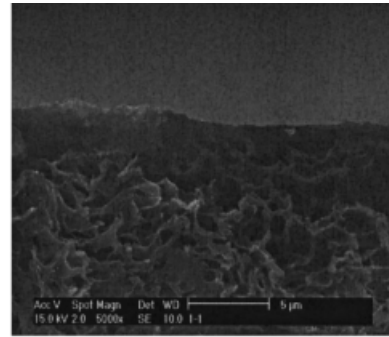
Different weight percent of PEI was dissolved at 60°C with stirring in solvent mixture (DMF and 1,4-dioxane). The weight ratio of DMF and 1,4-dioxane was changed. The clear casting solution was kept at room temperature for 24 h. Air bubbles in the casting solution were removed by keeping them for five days without stirring at room temperature. The casting solution was cast on a polyester nonwoven fabric with a doctor knife having 200 μm thickness. The nascent membrane was immersed in a DI water coagulation bath without evaporation of solvents in the air. After the immersion, the membranes were washed with flowing tap water for at least 12 h to remove solvent mixture.

Determination of Coagulation Value and Viscosity

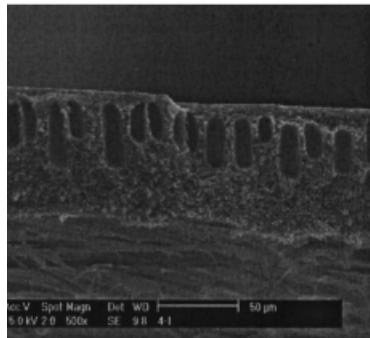
Coagulation value was measured to evaluate thermodynamic stability of casting solution (non-solvent tolerance). Polymer solution was prepared by dissolving 1 g PEI in 99 g of the DMF/1,4-dioxane solvent mixture. The polymer solution was placed in $30 \pm 1^\circ\text{C}$ water bath and titrated with DI water until the clear polymer solution



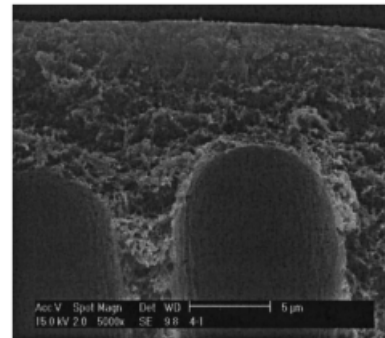
(a)



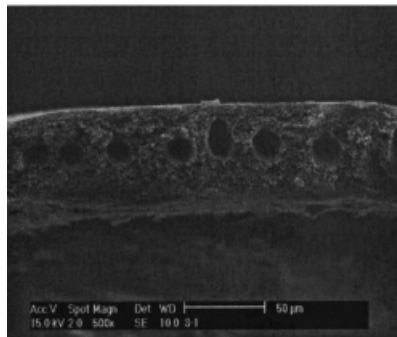
(a-1)



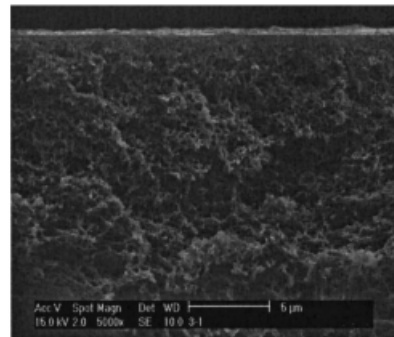
(b)



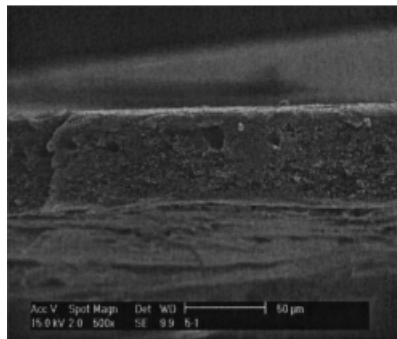
(b-1)



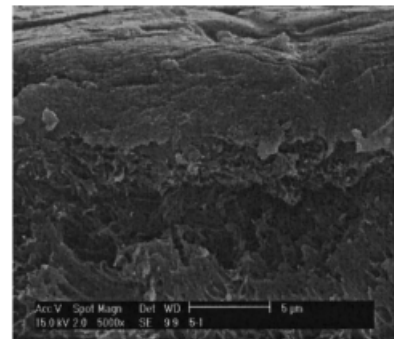
(c)



(c-1)



(d)



(d-1)

became turbid and was not redissolved in 24 h at that temperature. Viscosity was measured by Rheometer at 30°C to investigate the state of each polymer solutions.

Morphology of Asymmetric Membranes

Membrane morphology (cross section, top layer) was observed with a scanning electron microscope (SEM, JSM 1025, JEOL). The membrane was cryogenically fractured in liquid nitrogen and then coated with gold.

Membrane Performance Measurement

The PEG 600 (Showa) solution flux was measured at 200 psi, 2.5 L/min of flow rate and 25°C. The solute rejection rate was measured with poly(ethylene glycol) (PEG) 600 at the same condition above. The feed concentration was 1000 ppm in pure DI water. The permeate concentration was measured by HPLC (Waters Co.) equipped with a refractometer.

RESULTS AND DISCUSSION

Polymer solution properties

The effect of 1,4-dioxane on polymer solution properties (viscosity and coagulation value) was studied. In concentrated polymer solution, viscosity decreases with the strength of the polymer-solvent interaction. Therefore, the viscosity is lower in good solvents than in poor solvents. Coagulation value is a good index for understanding polymer solution properties. In other words, by increasing the solvent power, the coagulation value increases. The more nonsolvent required, the greater the solvent power. Figure 1 shows the viscosity and the coagulation value changes at different mass ratio of 1,4-dioxane to DMF. With increasing the content of 1,4-dioxane in polymer solution, viscosity was slightly increased. However, coagulation value was drastically increased. This phenomenon shows that 1,4-dioxane works as a cosolvent additive for PEI. 1,4-Dioxane increased the solvent power. This indicates that the polymer-polymer interaction was lowered, and

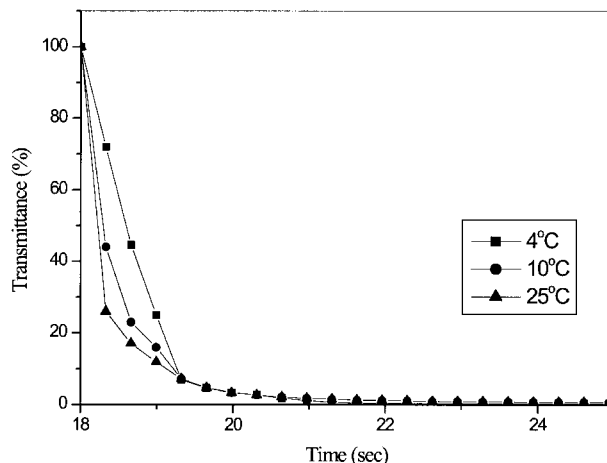


Figure 4 Effect of coagulation bath (water) temperature on light transmission experiments: PEI/DMF/1,4-dioxane (16/28/56 wt %).

instead the polymer-solvent interaction increased. In a good solvent system (containing cosolvent) polymer-solvent interaction is much greater than polymer-polymer intermolecular and intramolecular interactions.

Effect of 1,4-dioxane on membrane morphology

Generally, the membrane morphology can be characterized by the light transmittance measurement. In case of delayed liquid-liquid demixing, a sponge-like structure can be formed and in case of instantaneous demixing finger-like structure can be formed. Figure 2 shows that by increasing the amount of 1,4-dioxane in PEI/DMF solution, the polymer solution system is shifted from instantaneous demixing to delayed demixing process. This is due to the lower affinity of 1,4-dioxane with water than DMF. For delayed demixing, a dense skin layer is formed, which inhibits the inflow of water into the polymer solution. In the case of delayed demixing, the number and the size of nuclei of polymer-poor phase become smaller. Therefore, macrovoids are significantly disappeared. This trend can be supported by Figure 3. Without the addition of 1,4-dioxane, large fingers were shown because of instantaneous demixing. And the upper part of the mem-

Figure 3 SEM photographs of the cross section of PEI prepared from 16 wt % polymer solution: (a) overall, DMF alone; (a-1) upper part, DMF alone; (b) overall, 1,4-dioxane/DMF (1/1); (b-1) upper part, 1,4-dioxane/DMF (1/1); (c) overall, 1,4-dioxane/DMF (2/1); (c-1) upper part, 1,4-dioxane/DMF (2/1); (d) overall, 1,4-dioxane/DMF (3/1); (d-1) upper part, 1,4-dioxane/DMF (3/1).

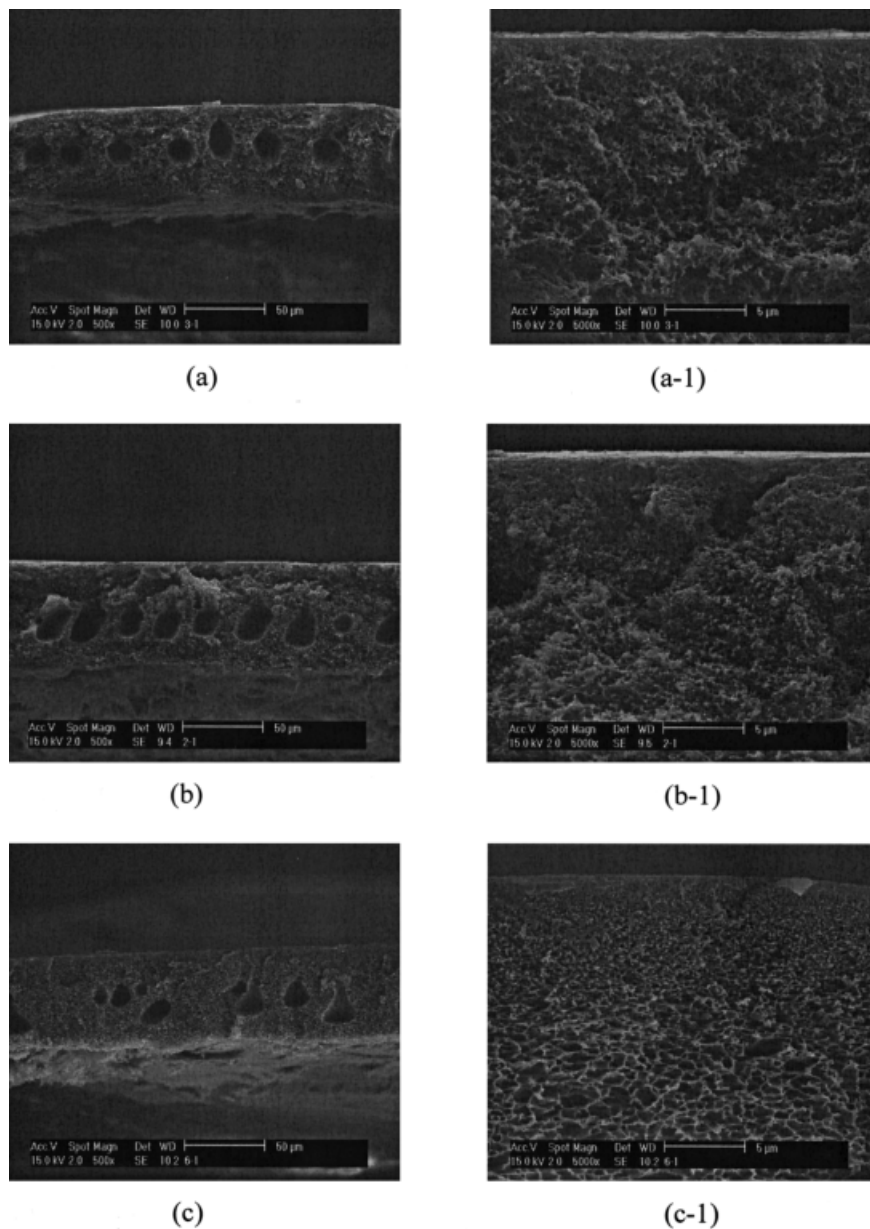


Figure 5 SEM photographs of the cross section of PEI prepared from PEI/DMF/1,4-dioxane (16/28/56 wt %) solution at different coagulation bath temperature: (a) overall, 4°C; (a-1) upper part, 4°C; (b) overall, 10°C; (b-1) upper part, 10°C; (c) overall, 25°C; (c-1) upper part, 25°C.

brane was porous. By increasing the amount of 1,4-dioxane, the number of macrovoids became smaller. And the top layer shows a very packed and dense shape. When the ratio of DMF to 1,4-dioxane was 1/3, almost all the macrovoids disappeared.

Coagulation temperature is an important parameter to affect membrane morphology and performance. Higher coagulation temperature makes the affinity between 1,4-dioxane and water better.

Light transmittance experiment of Figure 4 shows that with an increase in coagulation temperature, demixing pattern of the casting solution was gradually shifted from delayed demixing to instantaneous demixing. As shown in Figure 5, when the casting solution [PEI/DMF/1,4-dioxane (16/28/56)] was coagulated at the temperature of 25°C, porous spongy-like structure was shown. However, lower coagulation temperature (<10°C) makes the membrane structure dense spongy.

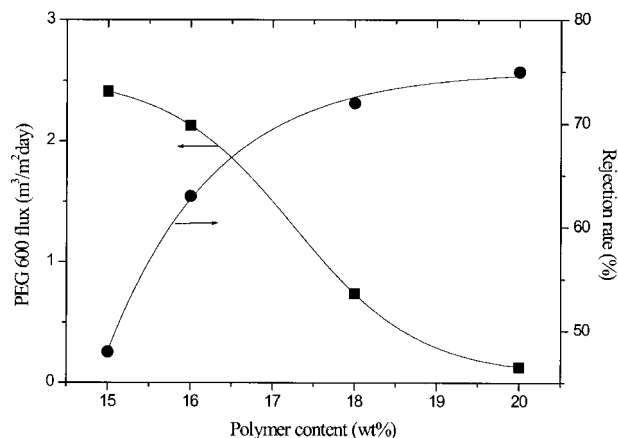


Figure 6 Effect of polymer concentration on the membrane performance: 1,4-dioxane/DMF (2/1), 4°C DI water (coagulant), 0 s evaporation time.

Membrane Performance

The effect of casting condition (coagulation bath temperature and evaporation time) and casting solution (polymer concentration and 1,4-dioxane content) on membrane performance was studied.

Figure 6 shows the membrane performance at different polymer concentration. The ratio of DMF to 1,4-dioxane and coagulation temperature was 1/2 and 4°C, respectively. The permeability of the membrane prepared from 18 and 20 wt % polymer solution was sharply decreased. Moreover, the rejection rate of the membrane was slightly increased. This result clearly indicates that although the pore size of the membrane was slightly reduced, porosity of the membrane was significantly decreased, while membrane prepared from 16 wt % polymer dope exhibited moderate permeability and rejection rate. In the case of the membrane prepared from 15 wt % polymer solution, the rejection rate was sharply decreased, whereas the increase in permeability was small. Increasing the polymer concentration in the casting solution leads to a much higher polymer concentration at the interface. This implies that the volume fraction of polymer increases and consequently a lower porosity is obtained.

The solvent evaporation time was varied from 0 to 30 s. Figure 7 exhibits the membrane performance resulting at different evaporation times. When the evaporation time was over 10 s, the permeability drastically decreased, whereas the rejection rate of PEG 600 was not changed. This is due to the incipient nucleation during evaporation period. The water vapor in the air makes the cast film phase separated. In other words, the cast surface of

the casting solution can be converted from clear one-phase solution into a turbid two-phase solution. This turbid surface inhibits the gelation, and consequently acts as a barrier against subsequent interdiffusion of solvent and nonsolvent in the bulk of the forming membrane. Therefore, the porosity and the permeability decrease as the evaporation time increases. As a result, increasing the evaporation time prior to immersion in the nonsolvent medium causes a porosity decrease and hence a decreases in permeability.

The PEI membrane prepared from DMF is not suitable to be used in nanofiltration application containing small molecules due to its excessively large pore size. In order to decrease the void volume, the additive should be added in casting solution. Especially, the miscibility of the additive with water should be poor compared to that of DMF. Additives such as tetrahydrofuran (THF), acetone, and 1,4-dioxane are good examples. In this study, we chose 1,4-dioxane as an additive. The small addition of THF and acetone as an additive makes the casting solution very unstable. However, as shown in Figure 1, 1,4-dioxane acts as a cosolvent, and a large amount of 1,4-dioxane can be added. Figure 8 shows the membrane performance with an increase of 1,4-dioxane content. As the concentration of 1,4-dioxane increased, the rejection rate of PEG 600 drastically increased because of the slower inflow diffusion of water into casting solution compared to DMF only. This result is due to the worse miscibility of 1,4-dioxane with water than DMF alone. Therefore, in order to decrease pore size of membranes, 1,4-dioxane as an additive in polymer solution can be suitable.

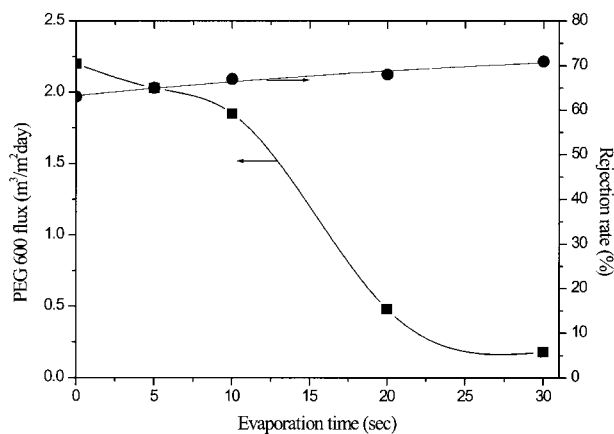


Figure 7 Effect of evaporation time on the membrane performance. PEI/DMF/1,4-dioxane (16/28/56), 4°C DI water (coagulant).

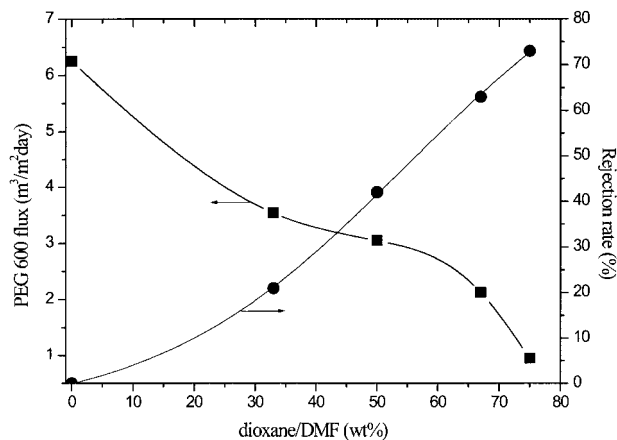


Figure 8 Effect of 1,4-dioxane content on the membrane performance: 16 wt % PEI, 4°C DI water (coagulant), 0 s evaporation time.

The casting solution with PEI/DMF/1,4-dioxane (16/28/56 wt %) was used to investigate this effect. The temperature of the coagulation bath was varied from 4 to 25°C. Figure 9 shows the membrane performance obtained at the various coagulation bath temperatures. As can be expected, with an increase of coagulation bath temperature to 25°C, rejection rate was decreased. This experimental data are due to the faster inflow diffusion of 25°C water than that of lower temperature water. An increase in the coagulation temperature seems to have a drastic influence on the performance. In other words, increasing temperature of coagulation bath hastens the onset of gelation, which in turn results in increased void size, degree of swelling, and permeability and decreased rejection rate.

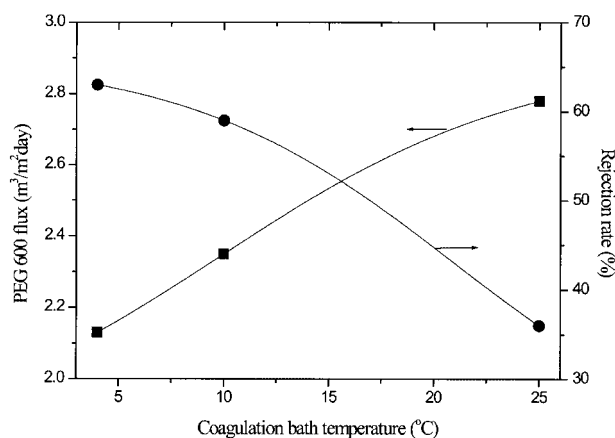
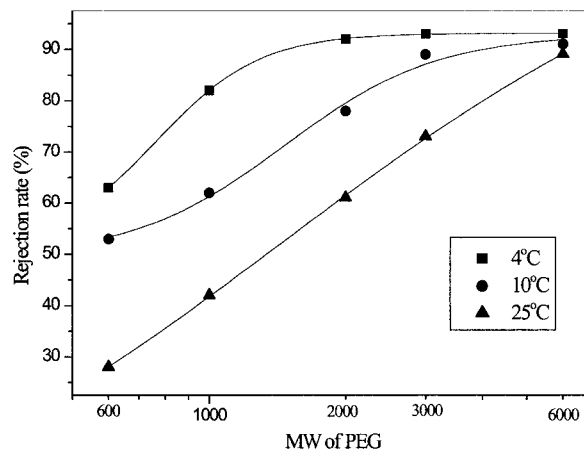
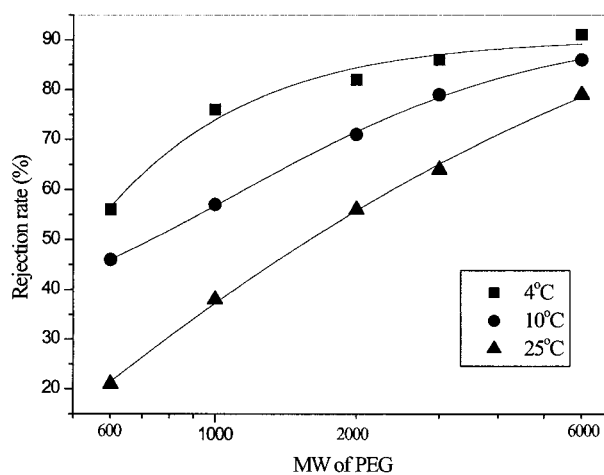


Figure 9 Effect of coagulation bath temperature on the membrane performance: PEI/DMF/1,4-dioxane (16/28/56), 0 s evaporation time.



(a)



(b)

Figure 10 Rejection rate of membrane for different molecular PEG at different operating pressures: (a) 45 psi and (b) 200 psi. PEI/DMF/1,4-dioxane (16/28/56), 0 s evaporation time.

Figure 10 shows the rejection properties of PEI membrane prepared from the casting solution [PEI/DMF/1,4-dioxane (16/28/56 wt %)] at different coagulation bath temperatures. The operating pressure was 45 and 200 psi, respectively. When operated at lower pressure (45 psi, ultrafiltration region), the molecular weight cutoff (MWCO) value was PEG 1000 (coagulation bath temperature of 4°C). By increasing the coagulation bath temperature, MWCO was shifted to PEG 3000 (10°C) and PEG 6000 (25°C), respectively. When

operated at higher pressure (200 psi, nanofiltration region) the MWCO was PEG 3000 (coagulation bath temperature of 4°C). And MWCO of other membranes coagulated at higher temperature was higher than PEG 6000. The drop in solute rejection at higher pressure is typical for porous membranes. This is due to the increase of solute concentration at the concentration polarization layer. The buildup of solute on the membrane surface results in faster solute transfer rate through the membrane at higher pressure compared to that of lower pressure.

CONCLUSIONS

Integrally skinned asymmetric PEI membranes were prepared from casting solution containing PEI, DMF, and 1,4-dioxane. The PEI membrane having small pore size and marginal flux was successfully made from the casting solution [PEI/DMF/1,4-dioxane (16/28/56)] by the phase-inversion process using water as a coagulant. 1,4-Dioxane as an additive was suitable for decreasing pore size. From viscosity and coagulation value data, it revealed that 1,4-dioxane works as a cosolvent. The membrane morphology with small pore size was a spongy-like structure with a small number of macrovoids. And the skin layer shows dense structure. It was also found that with increasing the polymer concentration in the casting solution, permeability was significantly decreased. And the solvent evaporation was not suitable to control the pore size and porosity of membranes. The molecular weight cutoff of the PEI membrane was ~1000 Daltons. With an increase of coagulation bath temperature, the pore size increased.

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