Effect of Various Additives on Pore Size of Polysulfone Membrane by Phase-Inversion Process

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ABSTRACT: The phase-inversion process was used to prepare integrally skinned asymmetric polysulfone (PSf) membranes with different pore sizes. Membranes were prepared from a casting solution of PSf; *N*-methyl-2-pyrrolidone (NMP) as solvent; and 1,4-dioxane, diethylene glycol dimethyl ether (DGDE), acetone, and γ-butyrolactone (GBL) as additives by immersing them in water as a coagulant. The effect of the additives on membrane performance and structure was investigated. The low miscibility of 1,4-dioxane, DGDE, and acetone with the coagulant resulted in reduced membrane pore size. However, by using GBL as additive pore size of the membrane was slightly increased because of its higher miscibility with the coagulant than NMP. Changing the amount of additives in the casting solution could control the molecular-weight cutoff values of asymmetric membranes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2562–2566, 2003

Key words: polysulfone; membranes; 1,4-dioxane; diethylene glycol dimethyl ether; acetone; γ-butyrolactone; miscibility; additives

INTRODUCTION

Various grades (different pore sizes) of asymmetric membranes have been developed because of the necessity of having membranes with different separation areas. Among several polymeric materials, polysulfone (PSf) has been widely used as an polymer for commercial ultrafiltration and microfiltration membranes. Moreover, PSf has been used for support material of nanofiltration and reverse osmosis membranes because of its high chemical stability, excellent mechanical properties, and resistance to microorganisms.

Asymmetric membranes, which are composed of a dense top layer and a porous support layer, traditionally are prepared using the phase-inversion method.[1–4] According to this method, a casting solution is precipitated in a coagulation bath. Membrane surface properties (pore size and porosity) depend on the relative diffusion rate of solvent and coagulant. Changing the casting solution composition,[5–14] casting conditions,[15–17] and coagulation bath composition[18] can control the diffusion rate. The diffusion rate is defined as the ratio of nonsolvent inflow to solvent outflow. If solvent outflow velocity in the casting solution toward the coagulation bath is faster than nonsolvent inflow velocity toward the casting solution, a membrane with a smaller pore size and a denser skin layer is formed. Among various methods for controlling membrane performance and structure, the addition of the secondary component (cosolvent or nonsolvent) in the casting solution can be a convenient and effective way.

In this study we prepared asymmetric PSf membranes with different performances by adding 1,4-dioxane, diethylene glycol dimethyl ether, acetone, and γ-butyrolactone to the casting solution. And the effects of various additives in PSf casting solution on membrane performance and structure were investigated.

EXPERIMENTAL

Materials

Polysulfone (PSf, Udel® P 3500, Amoco, Marietta, OH) was used as membrane material. The polymer was dried for at least 5 h at 100°C before being used in preparing the casting solution. *N*-Methyl-2-pyrrolidone (NMP, Aldrich, Milwaukee, WI) was used as a solvent. 1,4-Dioxane, diethylene glycol dimethyl ether (DGDE), acetone and γ-butyrolactone (GBL) were kindly supplied from Aldrich and used as additives. Deionized (DI) water was used as a coagulation medium. All chemicals were used without further purification.

Membrane preparation

PSf (15 wt %) was dissolved in the NMP/additive mixture at 60°C with stirring. The weight ratio of

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NMP to additive was changed. The casting solution was kept at room temperature for at least 24 h in order to remove air bubbles. The casting solution was cast on a polyester nonwoven fabric with a doctor's knife 200 μm thick. The nascent membrane was immersed in a DI water coagulation bath within 10 s. After immersion the remaining solvent mixtures were removed by keeping them in tap water for at least 24 h.

Determination of coagulation value and viscosity

The coagulation value was measured to evaluate the thermodynamic stability of the casting solution (nonsolvent tolerance). The polymer solution was prepared by dissolving 1 g of PSf in 99 g of the NMP/additive mixture. The polymer solution was placed in a 30°C ± 1°C water bath and titrated with DI water until the clear polymer solution became turbid and was not redissolved in 24 h at that temperature. Viscosity was measured by a rheometer at 30°C to investigate the state of each polymer solution.

Membrane performance measurement

Membrane performance was measured at 200 psi, with a flow rate of 1.0 L/min and temperature of 25°C. The solute rejection rate was measured with poly(ethylene glycol) (PEG) 12000 and 35000, polyvinylpyrrolidone 40000, and dextran 87000 at different pressures. The feed concentration was 1000 ppm in pure DI water. The concentrations of permeated and feed solutes were measured by a high-performance liquid chromatograph (Waters Co.) equipped with a refractometer. The rejection rate (R) was defined as R (%) = $(1 - C_p/C_f) \times 100$, where C_f and C_p denote the concentrations of feed and permeate, respectively.

Structure of asymmetric membranes

Membrane structure (cross section and 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.

RESULTS AND DISCUSSION

Polymer solution properties

Table I shows the effect of various additives on polymer solution properties using 1,4-dioxane, DGDE, acetone, and GBL. The addition of 1,4-dioxane, DGDE, and acetone in the casting solution was able to reduce the viscosity, which means those materials were cosolvents for the system. In contrast, with the addition of GBL to the casting solution, the viscosity of the casting solution was observed to be higher than that of the casting solution in the absence of this additive. In

TABLE I
Effect of Various Additives on Polymer Solution Properties

Ratio of NMP to additive in 15 wt % PSf solution		Viscosity (cP)[a]	CV (g)[b]
No additive		371	9.23
NMP	1,4-dioxane		
57	28	316	9.58
41	43	349	9.94
28	57	304	10.59
NMP	DGDE		
57	28	310	9.38
41	43	294	9.64
28	57	297	9.85
NMP	Acetone		
57	28	199	9.68
41	43	247	10.04
28	57	—[c]	—
NMP	GBL		
57	28	505	8.94
41	43	577	8.32
28	57	714	8.11

[a] Polymer concentration: 15 wt %.
[b] Coagulation value: 1 wt % of polymer concentration.
[c] At this composition polymer solution could not be prepared.

other words, for the system GBL seems to be a swelling agent or nonsolvent for the polymer, Generally, in a concentrated polymer solution, viscosity is lower in a good solvent than in a poor one, which means that the interaction between polymer and solvent becomes better than that between the polymer molecules. In a polymer solution system, which includes a poor solvent, the polymers form a network structure. The network structure prevents the flow of the polymer molecules. In other words, polymer molecules disturb each other. However, in a diluted polymer solution system, viscosity is higher in the good solvent than in the poor solvent. This is because of the stretched linear shape formation of each polymer molecule. And polymer molecules are unperturbed by each other.

Coagulation value (CV) is also a good index for understanding polymer solution property. In other words, with solvent power, the CV increases. The more nonsolvent is required, the greater is the solvent power. When 1,4-dioxane, DGDE, and acetone were used as additives, the CV was increased. However, GBL decreased the CV. This result matched well with that for viscosity. As a result, for 1,4-dioxane, DGDE, and acetone, the interaction between polymers decreased; instead, the interaction between polymer and solvent became greater. And for GBL and acetone, the interaction between polymers was greater and the interaction between polymer and solvent lowered.

Membrane morphology was characterized by SEM photography (Fig. 1). The shape of the cross section was not changed by the addition of additives to the casting solution,. In other words, the cross-sections
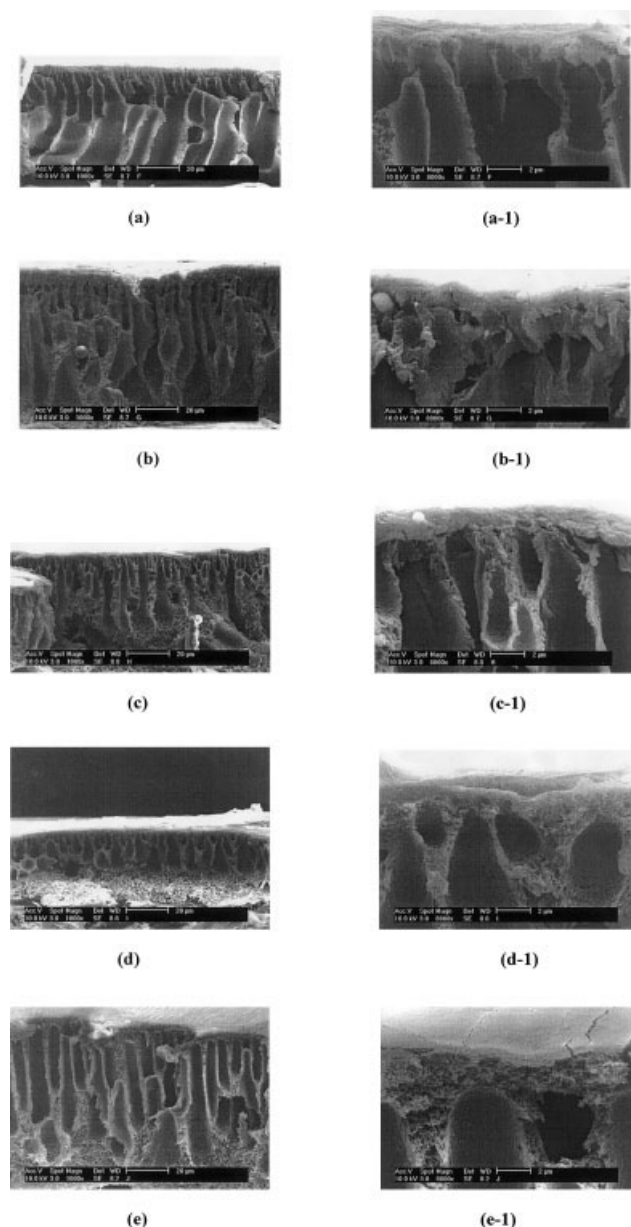
Figure 1 SEM photographs of cross section of PSf membrane prepared from 15 wt % PSf: (a) overall, NMP alone; (a-1) upper part, NMP alone; (b) overall, 1,4-dioxane/NMP (1:1); (b-1) upper part, 1,4-dioxane/NMP (1:1); (c) overall, DGDE/NMP (1:1); (c-1) upper part, DGDE/NMP (1:1); (d) overall, acetone/NMP (1:1); (d-1) upper part, acetone/DMF (1:1); (e) overall, GBL/NMP (1:1); (e-1) upper part, GBL/NMP (1:1).

showed that all the membranes had fingerlike structures with or without additives. However, the shape of the top layer was different. As a consequence of adding additives such as 1,4-dioxane, DGDE, and acetone, the top layer became denser and thicker than its counterpart in membranes without additive. For GBL, the porous sponge structure of the top layer was observed.

Membrane performance

Figure 2 shows the rejection rate difference of various polymeric molecules at different operating pressures. Even though the molecular weight of polyvinylpyrrolidone (PVP) is smaller than that of dextran, the rejection rate was much greater. This is because of the larger Stokes–Einstein radius of PVP 40000 than of dextran 87000. Moreover, the stickiness of PVP 40000 could be another reason for its higher rejection rate. The drop in solute rejection rate at higher pressures is typical for porous membranes. This is because of the increase in solute concentration at the concentration polarization layer. The buildup of solute on the membrane surface results in a faster solute transfer rate through the membrane at higher pressure compared with that at lower pressure. We chose PEG 35000 as the feed solute for investigating the pore size change with different additives and compositions.

Figure 3 shows the rejection rate of PSf membranes with and without additives in the casting solution. Among the various additives, 1,4-dioxane, DGDE, and acetone can decrease pore size. With an increasing amount of additives, the rejection rate of solute was increased. However, GBL was not able to affect pore size. Increasing the amount of GBL could not increase the rejection rate. These results were consistent with that observed in the SEM photographs. In other words, additives like 1,4-dioxane, DGDE, and acetone can play the role of a pore reducer in the top layer to increase the rejection rate of the PSf membranes. This is because of the miscibility of the additive with the coagulant. The miscibility of 1,4-dioxane, DGDE, and acetone with water might be poor compared with that of NMP, as shown in Table II, which has a comparison of each solubility parameter [dispersion (δ_d), polar (δ_p), and hydrogen bond solubility parameter (δ_H)]. As
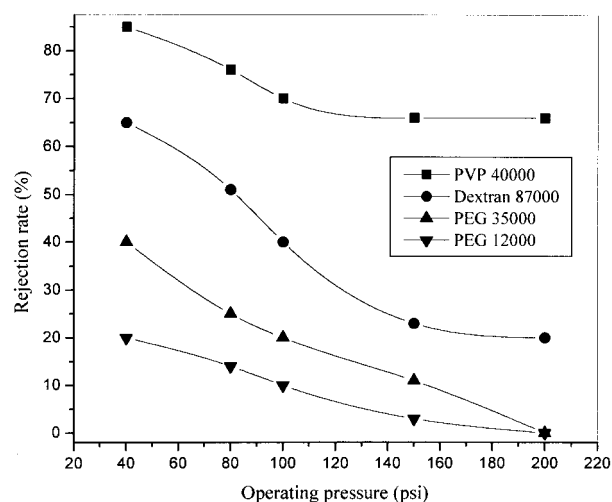

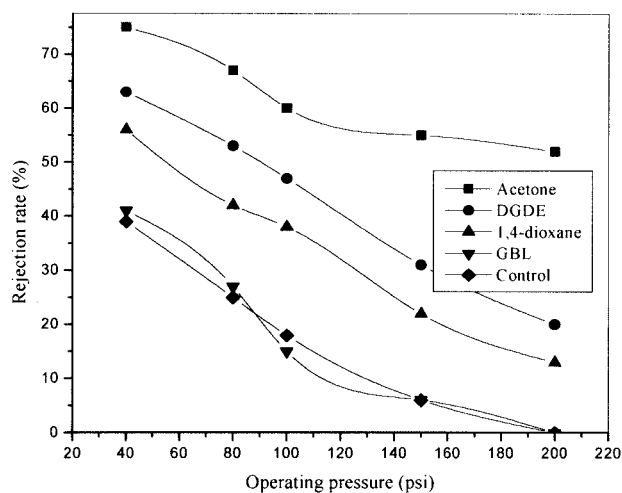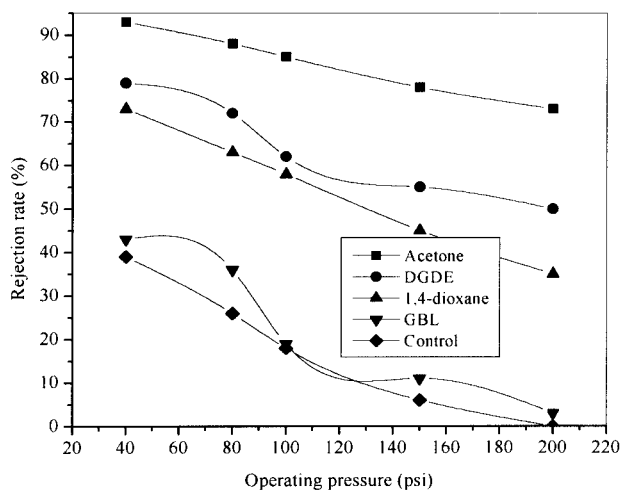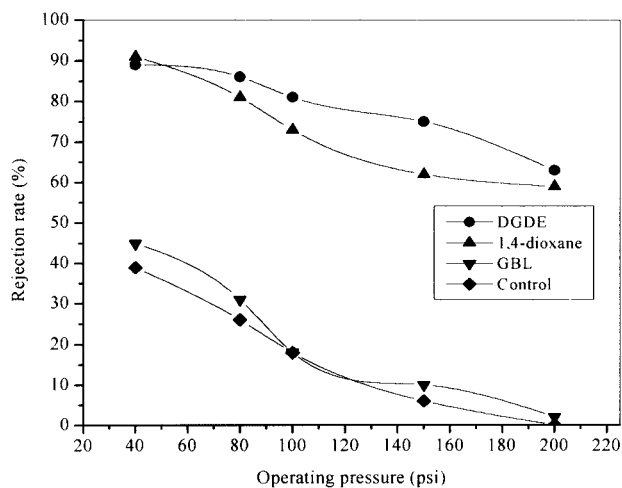**Figure 2** Rejection rate of the control of the feed solution containing different solutes at different operating pressure.

Figure 3 Effect of various additives and amounts on the rejection rate at different operating pressures: (a) additive/NMP (0.5:1); (b) additive/NMP (1:1); (c) additive/NMP (2:1).

TABLE II
Solubility Parameters of Various Solvents

Solvents	Solubility parameter		
	δ_d (MPa$^{0.5}$)	δ_P (MPa$^{0.5}$)	δ_H (Mpa$^{0.5}$)
NMP	18.0	12.3	7.2
Water	15.5	16.0	42.4
1,4-dioxane	19.0	1.8	7.4
Acetone	15.5	10.4	7.0
GBL	19.0	16.6	7.4
DGDE	15.8	6.1	9.2

can be seen, the dispersion solubility parameters are similar to each other. And the hydrogen bond solubility parameter of water is too large to compare with NMP and other various additives. Therefore, we compared the polar solubility parameter. If the polar solubility parameter of an additive is larger than that of NMP, the additive is more miscible with water than would be NMP alone. This means that a polar solubility parameter value of an additive that is smaller than that of NMP can be only slightly miscible with water compared with NMP. As shown in Table II, the polar solubility parameter values of 1,4-dioxane, DGDE, and acetone are smaller than that of NMP. This implies that when a casting solution containing 1,4-dioxane, DGDE, and acetone is coagulated in water, the inflow rate of coagulant will become slower compared with that of NMP alone. In addition to this effect, DGDE can form a sharp interface with water. This can be attributed to the slower exchange rate of a polar solvent in the coagulation bath than the inflow rate of water. This suggests that DGDE should inhibit water from entering the polymer solution. Even though the polar solubility parameter value of acetone was larger than that of 1,4-dioxane, the rejection rate was much greater. This is because of its relatively lower boiling point. This resulted in rapid loss of acetone during casting.

However, for GBL, the polar solubility parameter value was much larger than NMP. This implies that the entering rate of water in the casting solution was faster than NMP alone. Therefore, by using GBL as an additive, a more porous membrane could be formed.

When 1,4-dioxane, DGDE, and acetone were used as additives, the top layer had a very packed and dense shape because of the lower miscibility with water compared with NMP alone. Moreover, the sponge cells were closed. However, using GBL as an additive rendered the top layer more porous. The size of the sponge became bigger and opened as a result of its higher miscibility with water compared with NMP only.

CONCLUSIONS

Asymmetric PSf membranes could be prepared by the phase-inversion method from a casting solution con-

taining polymer, NMP, and additives (1,4-dioxane, DGDE, acetone, and GBL). The viscosity and coagulation values showed that 1,4-dioxane, DGDE, and acetone can play the role of cosolvent for the system and that GBL works as a swelling agent or nonsolvent. Adding 1,4-dioxane, DGDE, acetone, and GBL to the casting solution in our study did not change the membrane cross-section shape; however, the top layer was found to have a very packed and closed structure. But when using GBL, the shape of the top layer was porous with an open sponge structure. The pore size of the membranes prepared from the casting solution containing 1,4-dioxane, DGDE, and acetone decreased. Yet when using GBL as an additive, the pore size could not be decreased.

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