Effects of Casting Solution Composition on Performance of Poly(ether sulfone) Membrane

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SYNOPSIS

Flat-type poly(ether sulfone) (PES) membranes for ultrafiltration were prepared by the traditional phase-inversion technique. The effects of the concentration of PES and the combination of two solvents, dichloromethane (DCM) and N-methyl-2-pyrrolidone (NMP), with differences in volatility and solvating power on membrane performance were examined in terms of pure water flux (PWF) and solute rejection (SR) against poly(ethylene glycol) (PEG, MW 20,000). Changing the thermodynamic quality of PES/NMP casting solution by combining DCM, a volatile and weak solvent, affected the PWF of the resulting membrane. The SR of PES/DCM–NMP membrane, however, was more likely dependent upon the effect of evaporating the volatile solvent from the casting solution/air interface rather than the effect of changing the thermodynamic quality of the casting solution. Combining DCM in PES/NMP casting solution transformed the fingerlike macrovoids of PES/NMP membrane prepared without DCM into the isolated macrovoids. PES/DCM–NMP membrane prepared with PVP, a water soluble pore-forming agent, showed an increased PWF while maintaining SR of over 90%, even under the reduced feeding pressure of 1 kg/cm². It is necessary to measure molecular weight cutoff of membrane for demonstrating the potential of PVP for improving the membrane permeability without losing the selectivity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The permselectivity of an asymmetric membrane prepared via the phase-inversion process[1,2] is generally controlled by the thin "skin" structure formed at the top surface layer of the membrane. The skin structure is generally formed from the increased polymer concentration at the casting solution/air interface at the point of precipitation. It is therefore expected that evaporating the solvent from the interface before precipitating the polymer can increase the polymer concentration at the top surface layer so that the formation of the skin structure can be expedited.

Dimethylformamide (DMF), dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP) have been widely used as solvents for membrane polymers. It is not easy, however, to evaporate those solvents from the casting solution/air interface owing to their poor volatilities. Therefore, the forced evaporation process was considered: the reduced pressure, the high temperature, or the prolonged evaporation period. However, none of those were desirable in view of the technical difficulty and the reproducibility of the membrane.

We were interested in removing the considerable amount of solvent from the interface for a short evaporation period. Our specific interest was in the use of the combination of two solvents with differences in volatility and solvating power.[3–8] In this study, poly(ether sulfone) (PES) asymmetric membranes were prepared with a cosolvent system of dichloromethane (DCM) and NMP as volatile and

nonvolatile solvent, respectively. The combination of two solvents was designed for partially removing more volatile solvent from the interface by evaporation, so that the skin layer formed at the top of the membrane could have a fine structure providing high permselectivity of the membrane. PES solubility in the solvent system was controlled by changing the combining ratio of DCM and NMP because PES dissolved differently in these solvents. The effect of poly(vinyl pyrrolidone) (PVP), a water soluble pore-forming agent, in the casting solution was examined in terms of pure water flux (PWF) and solute rejection (SR) of the membrane. The prime interest for using PVP was to enhance membrane permeability while minimizing the loss of membrane selectivity.

EXPERIMENTAL

Materials

Membrane casting solutions were composed of PES (4800P, MW 22,400, ICl, U.K.) used as the membrane polymer dissolved in the combinations of DCM (Junsei, Japan) and NMP (Aldrich, U.S.A.). Boiling temperature and vaporizing pressure of the two solvents were 39.75°C and 348.9 mmHg at 20°C for DCM, and 202°C and 4 mmHg at 60°C for NMP, respectively. DCM and NMP were miscible with each other. PVP (MW 10,000, Aldrich) was added to the casting solution as a water soluble pore-forming agent.

Polymer Solubility

The mixture of PES (20% w/v) in DCM, NMP, or their combination was sealed and stored for 48 h under shaking at 20°C. PES solubility was determined by visually observing the clarity of the mixture. Different from being dissolved completely in NMP, PES was swollen sufficiently in DCM. PES solubility in the DCM-NMP mixture was, therefore, according to the combination of the two solvents.

Preparation of Asymmetric Membrane

Flat-type PES membrane was prepared by machine casting. The polymer solution was formed onto the 200-μm thick membrane on a glass plate in the chamber in which the atmospheric temperature and the relative humidity were fixed at 25°C and 35 ± 5%, respectively. To evaporate solvent from the

casting solution/air interface, the cast film was exposed to the air in the chamber. After evaporating the solvent from the interface, the nascent membrane was immersed into a cold water bath (4°C) for coagulation. The solidified membrane was stored in the same bath for 2 h. The membrane was transferred into the running water and kept for 24 h to completely remove the residual solvent from the membrane. The resulting membrane was cut into a desired shape for a test kit, and stored in cold water.

Membrane Performance

Membrane permeability was examined with Amicon®-8200 stirred batch cell in terms of PWF and SR. A 1000 ppm aqueous solution of poly(ethylene glycol) (PEG, MW 20,000, Waco, Japan) was used for determining the SR of the membrane. SR was analyzed by the following equation:

$$\text{SR (\%)} = (1 - C_p/C_f) \times 100$$

where C_f is the PEG concentration in the feed solution and C_p is the PEG concentration in the product solution. PEG concentrations were measured with the Carbon Analyzer (Beckman Total Organics, 915B).

Morphological Studies

PES membrane was cryofractured, sputter coated with gold, and examined with an Akashi DS-130 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Effect of PES Concentration

PES membranes were prepared with the solutions of up to 25% (w/v) PES. Polymer concentration lower than 17% (w/v) PES was excluded owing to the low viscosity. The membrane prepared with over 22% (w/v) PES was excluded because of the negligible PWF.

PWF of PES membranes was larger when the membrane was prepared with a lower concentration of PES (Fig. 1). The 17% (w/v) PES membrane showed a PWF of 159 L/m² h, compared to the 22% (w/v) membrane, indicating much higher permeability of the former membrane. On the contrary, SR of PES membranes was higher when the membrane was prepared with a higher polymer concen-
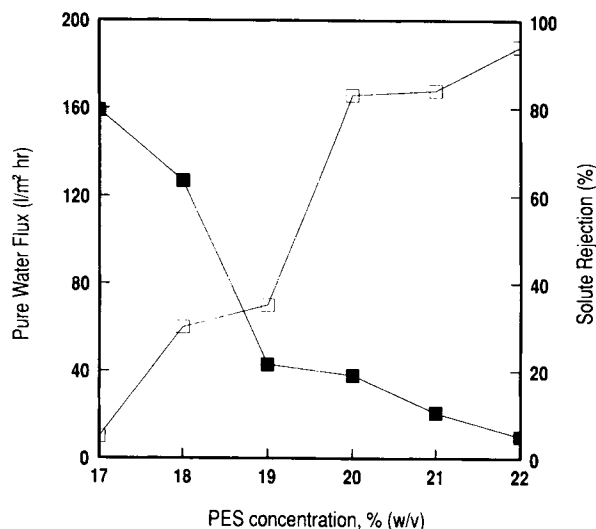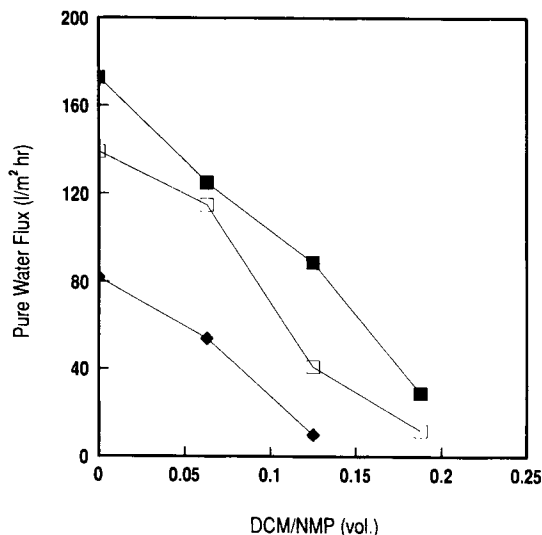
Figure 1 The effects of PES concentration on the (■) pure water flux and (□) solute rejection (against PEG 20,000) of PES/NMP membrane. Solvent was evaporated from the casting solution/air interface for 1 min before coagulation.

Figure 2 Pure water flux of 20% (w/v) PES membranes prepared with different combinations of DCM and NMP. The effect of solvent evaporation period is also shown: (■) 0 min, (□) 0.5 min, and (◆) 1 min.

tration. For example, 22% (w/v) PES membrane exhibited the highest SR of 94% against PEG 20,000. High polymer concentration of the initial casting solution tends to increase the polymer concentration at the casting solution/air interface at the point of precipitation. Thus, dense skin structure would be formed at the top surface layer of the membrane that provides low PWF but high SR.[2]
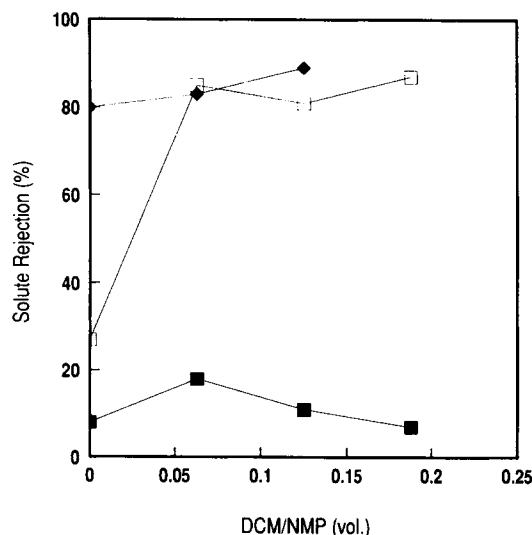
Combinations of Cosolvent

PES solutions used for preparing 20% (w/v) PES membranes were made with various combinations of DCM and NMP of up to a 0.375 volumetric fraction of DCM in their combination. Because DCM was a weak solvent for PES, it was expected that the thermodynamic quality of PES/DCM–NMP solution would be decreased with the increase of DCM. The solution of higher fraction of DCM than 0.375 was excluded because the solution lost the clarity.

PWF of PES membranes was smaller when a larger fraction of DCM was used to prepare the membrane (Fig. 2). SR of PES membranes was, however, more likely dependent upon the solvent evaporation from the casting solution/air interface rather than the change of thermodynamic quality of the casting solution (Fig. 3). SR was steeply increased when the membranes were prepared with solvent evaporation.

Figure 4 compares two different structures of PES membranes prepared with different combinations of DCM–NMP. Figure 4(a) shows the structure of PES membrane prepared with pure PES/NMP (without DCM) solution of high thermodynamic quality. Fingerlike macrovoids were well developed, which

Figure 3 Solute rejection (against PEG 20,000) of 20% (w/v) PES membranes prepared with different combinations of DCM and NMP. The effect of solvent evaporation period is also shown: (■) 0 min, (□) 0.5 min, and (◆) 1 min.

(a)   (b)
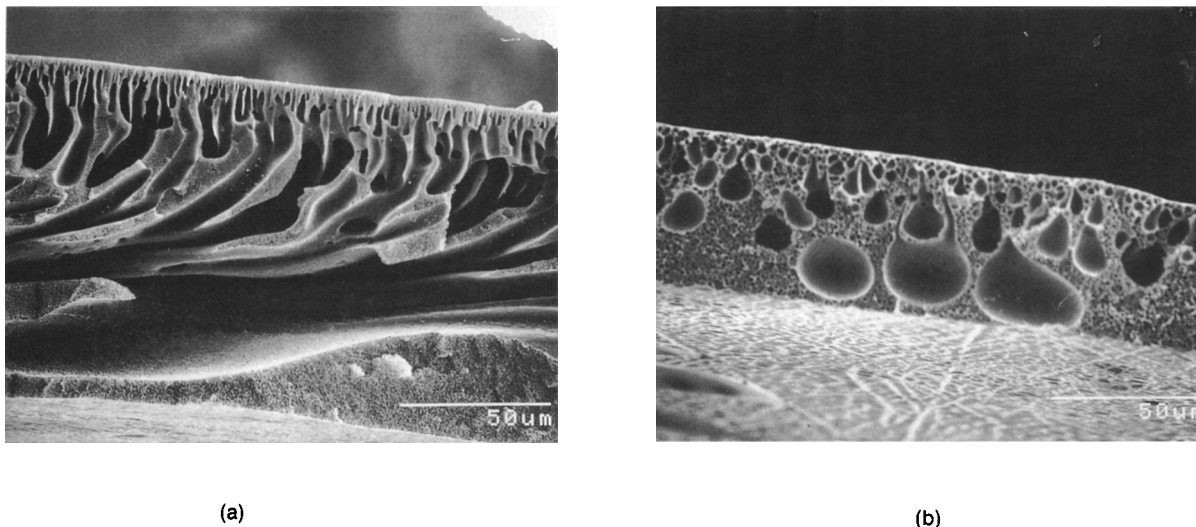
Figure 4   Scanning electron micrographs of the cross sections of 20% (w/v) PES membranes prepared with different combinations of DCM/NMP (taken at 600X). Volumetric fractions of DCM in combinations of DCM and NMP are (a) 0 and (b) 0.375.

is the typical structure of micro/ultrafiltration membranes of high permeability.[9]

Macrovoid formation can be described by the convective flow model[10] in which macrovoid is formed by sudden intrusion of nonsolvent through the skin structure of the membrane. On the other hand, macrovoid formation can also be explained by the growth of nuclei of the solvent-rich phase in polymer solution.[11] According to this model, macrovoid can grow quickly from the freshly formed nuclei of the solvent-rich phase as long as the polymer solution in front of the growing nuclei still has the stable composition. For that, a higher solvent content and/or a lower polymer concentration in polymer solution with high thermodynamic quality are favorable conditions, which demonstrates high PWF of PES/NMP (without DCM) membrane in Figure 2.

The decrease of the thermodynamic quality of the initial polymer solution prepared with the combination of the two solvents is attributed to the formation of membrane with low porosity.[8] Figure 4(b) shows the structure of the PES membrane prepared with PES/DCM–NMP solution (0.375 DCM fraction). Different from fingerlike structures in Figure 4(a), the macrovoids were isolated. Because the polymer solution was not stable, the polymer molecules contacting nonsolvent coagulant on immersion would tend to aggregate rapidly, subsequently forming the top surface layer composed of very high polymer concentration. The top surface layer,

therefore, can act as a diffusional barrier against the exchange of solvent and nonsolvent, and become the dense skin layer of the resulting membrane attributed to low PWF but high SR, demonstrating the results in Figures 2 and 3. Because the influx of nonsolvent coagulant through the top surface layer was retarded, the solvent of the polymer solution surrounding the nuclei slowly diffused into the nuclei of the solvent-rich phase rather than exchange rapidly with nonsolvent, expand the nuclei, and subsequently form the isolated macrovoids.

As indicated in the Experimental section, low relative humidity of 35 ± 5% was given to the casting solution/air interface in the chamber, which is favorable for evaporating the volatile solvent. The longer evaporation period applied to the casting solution presumably led to the removal of a larger amount of solvent from the interface. Polymer concentration at the interface, therefore, was increased so that the dense skin layer could be formed, which resulted in high SR as shown in Figure 3.

Effect of Pore-Forming Agent

For improving the SR, PES membranes were prepared with 25% (w/v) PES. PVP (MW 10,000), a water soluble pore-forming agent, was added to 25% (w/v) PES solution so that the resulting membrane would have considerable PWF, even though the membrane was prepared with a higher PES concentration. PVP was found to be soluble in PES/DCM–

NMP solutions. A considerable amount of PVP (0.8 PVP : PES ratio, w/w) was added to the 25% (w/v) PES casting solution. PWF and SR of the membrane were measured under the reduced feeding pressure to 1 kg/cm² because there was too much PWF to be measured under the feeding pressure of 3 kg/cm², presumably attributed to the effect of PVP.

The 25% (w/v) PES membranes showed higher PWFs under the reduced feeding pressure of 1 kg/cm² (Fig. 5) than the 20% (w/v) PES membrane tested under 3 kg/cm². It was very interesting that the SRs of 25% (w/v) PES membranes against PEG 20,000 were also improved over 90%.

PVP would presumably be leached out of the solidified polymer matrix of the membrane when the membrane was coagulated and washed.[12-14] It was suggested that the addition of PVP into the casting solution does not significantly change the initial polymer concentration comprising PES and PVP at the surface layer of the membrane at the point of precipitation.[15] Leaching out PVP from the membrane, therefore, results in many spaces subsequently forming the surface pores of the membrane. It was also visually proven that using PVP as a pore-forming agent does change the number of surface pores of the membrane rather than the size of the pores.[16] This presumably explains the improvement of PWF of the PES membrane prepared with PVP while maintaining SR over 90% against PEG 20,000. For demonstrating the potential use of PVP for enhancing membrane permselectivity, however, measurement of molecular weight cutoff is required.

CONCLUSION

PES dissolved in NMP or in combinations of DCM–NMP was formed into the membrane via the phase-inversion process. PES concentrations from 17 to 25% (w/v) in NMP were suitable to make flat-type membrane by machine casting. Under the feeding pressure of 3 kg/cm², PWF of 17% (w/v) PES membrane was 159 L/m² h, indicating much higher permeability than 22% (w/v) PES membrane. The latter membrane, however, showed the highest SR of 94% against PEG 20,000 for the ultrafiltration level.

With the increase of the volumetric fraction of DCM in polymer solution, PWF of PES/DCM–NMP membrane was steeply decreased. The SR of PES/DCM–NMP membrane was improved when the membrane was prepared by evaporating volatile solvent from the casting solution/air interface be-
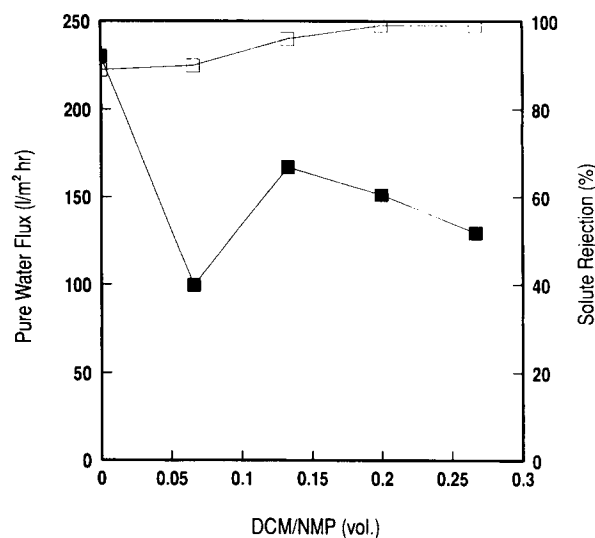
Figure 5 The effects of PVP (MW 10,000), a water soluble pore-forming agent, in the casting solution on the (■) pure water flux and (□) solute rejection of 25% (w/v) PES membrane prepared with different combinations of DCM and NMP. Solvent was evaporated from the casting solution/air interface for 1 min before coagulation.

fore precipitating polymer. Different from PES/NMP membrane where a fingerlike macrovoid was developed, PES/DCM–NMP membrane formed the isolated macrovoid.

PWF of 25% (w/v) PES membrane was rather improved, even under the reduced feeding pressure of 1 kg/cm², when the membrane was prepared with PVP (MW 10,000), a water soluble pore-forming agent. SR of PES/PVP/DCM–NMP membrane against PEG 20,000 was over 90%, which suggested that the membrane selectivity was maintained without losing the permeability.

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