

Morphology and Performance of Polysulfone Hollow Fiber Membrane

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SYNOPSIS

Polysulfone hollow fiber membranes were prepared via the dry-wet spinning process from dope solutions comprised of polysulfone, *n*-methyl-2-pyrrolidone, polyvinyl-2-pyrrolidone, and dodecylbenzene sulfonic acid, sodium salt. Morphology and performance of the membranes were affected by the compositions of coagulant and dope solution. Pore size and the water flux of the membrane increased by the addition of dodecylbenzene sulfonic acid, sodium salt to water in the coagulation bath, due to the changes of physicochemical properties of the outer coagulant. Addition of dodecylbenzene sulfonic acid, sodium salt to the dope solution also increased the pore size. The absence of polyvinyl-2-pyrrolidone, the pore forming agent, in the dope solution resulted in a remarkable decrease of pore size of the membrane. The distance between the spinneret and coagulation bath affected the membrane structure and performance. The membranes prepared in this study were suitable for hemofiltration in terms of molecular weight cut-off characteristics. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Several types of ultrafiltration and microfiltration membranes have been developed for applications in biological and food processes, as well as for medical devices, such as hemofiltration. Many polymeric materials have been developed, and some of them have been commercialized, such as cellulose, cellulose acetate, polyacrylonitrile, polysulfone, polyamide, polypropylene, and polyethylene.¹

Polysulfone (PS) has excellent properties as an ultrafiltration membrane, and it is commonly used. PS hollow fiber membrane was first made commercial by Amicon Co.,² and subsequently the copolymer polyether sulfone was developed, because of its better solubility as compared with polysulfone.³ Another modification was performed by sulfonating polysulfone to increase the hydrophilicity of the membrane.^{4,5} Another method for increasing the hydrophilicity of the membrane was proposed by adding

additives, such as poly(vinyl-2-pyrrolidone) (PVP), instead of the chemical modification of polymer.⁶ This method can also increase the diffusive transport properties of solute through the membrane.⁷

Phase inversion technique is generally used to fabricate the hollow fiber membranes. Depending on the phase separation mechanisms and the preparation procedures, each process was named as wet spinning, dry spinning, or melt spinning. At present, a combination wet and dry spinning process is employed in commercial polysulfone hollow fiber membrane production, and it is called a dry-wet spinning process. Precipitation of polymer can be initiated from inside, outside, or both sides of the hollow fiber, depending on the nature of the process, which determines the location of skin formation.

Although mechanisms of membrane structure formation via polymer precipitation have been investigated and some of them patented, there are still many operational parameters to be optimized.⁸⁻¹⁵ The parameters to be considered are: compositions of dope solution, kinds of bore coagulant and outer coagulant, the distance between the spinneret and the coagulation bath, temperature of coagulation

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bath, and so on. Exact effects of these parameters have not been clearly examined, due to the complex natures of the process and interdependencies of these parameters. Strathmann et al.¹⁶ have investigated the formation of cavities and intrusion cells within polyamide and polyacrylonitrile hollow fiber membranes, prepared via the dry-wet spinning process. Model and Lee¹⁷ investigated the formation of radial voids in polybenzimidazole hollow fiber membranes. Influences of various spinning parameters, as above, on the morphologies and transport properties of polysulfone hollow fiber membranes were examined by Cabasso et al.^{18,19}

In this study, structure variation by the addition of dodecylbenzene sulfonic acid, sodium salt (DBSS) to the outer coagulant or dope solution was considered in terms of their effects on the morphology and the performance of the polysulfone membrane. Effects of polyvinyl-2-pyrrolidone, a pore forming agent, and the air gap were also examined.

EXPERIMENTAL

PS (UDEL P-3500) was obtained from Amoco Co., and PVP (molecular weight = 10,000) was from GAF Corp. DBSS and *n*-methyl-2-pyrrolidone (NMP) were obtained from Aldrich Chemical Co. Polyethylene glycols (PEG) of various molecular weights were purchased from Wako Chemical Co., and dextrans of several molecular weights were purchased from Sigma Chemical Co.

Membrane Preparation

A dry-wet spinning apparatus was manufactured for the hollow fiber spinning, and its schematic diagram is shown in Figure 1. A homogeneous dope solution of polymer, solvent, and additives was metered to a spinneret of tube-in-orifice type, the inner and outer

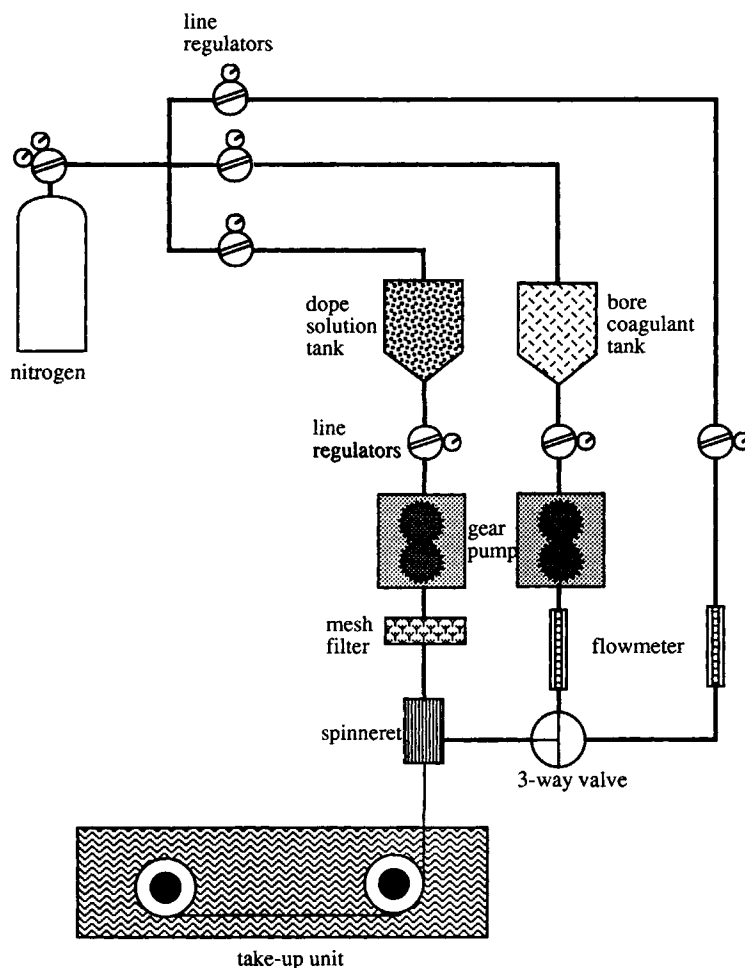


Figure 1 A schematic diagram of dry-wet spinning apparatus.

diameters of which were 0.40 mm and 0.70 mm, respectively.

The procedure for hollow fiber spinning is outlined in Figure 2. A homogeneous dope solution was prepared in a dope tank, then was filtered and supplied to the outer orifice of the spinneret. The metering rate was precisely controlled by a gear pump within the range of 5 to 30 mL/min. A bore coagulant was introduced into the inner tube of the spinneret at a corresponding rate to the dope solution feed rate. The distance between the spinneret and coagulation bath was defined as the air gap, and was varied from 0 to 120 cm. After the hollow fiber was solidified in the coagulation bath, it was wound on a take-up unit. All solvents and the other additive materials involved in the spinning process were completely washed out with water, and the membrane was stored in pure ethyl alcohol.

Examinations of Membrane Structure and Performance

Membranes were carefully dehydrated and fractured in liquid nitrogen to show the natural cross sections. Cross sections and surfaces of the membranes were

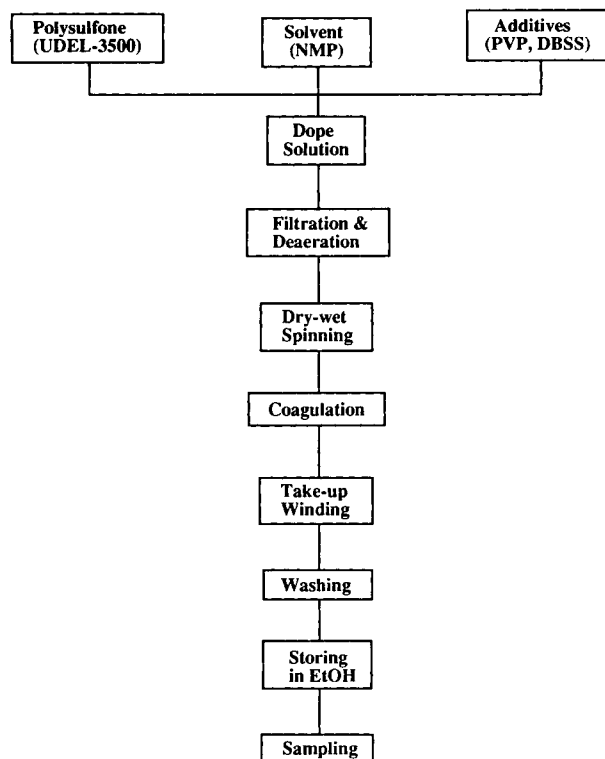


Figure 2 Procedures of polysulfone hollow fiber membrane preparation.

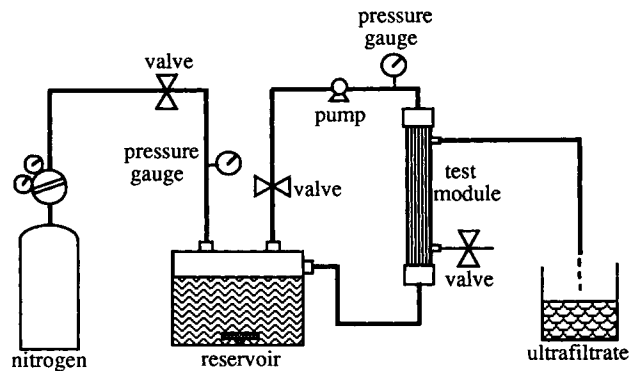


Figure 3 A schematic diagram of water flux measuring apparatus.

photographed using a scanning electron microscope (Hitachi, S-510).

Transport properties of the membranes were characterized by water flux measurements. Water flux at a steady state was measured with the apparatus shown in Figure 3 under the transmembrane pressure of 3 atm. PEGs and dextrans of various molecular weights were used as test solutes for measuring the molecular weight cut-offs of the membranes. Molecular weight of PEG ranged from 1,540 to 18,500 and that of dextrans from 9,500 to 72,600. Concentration of test solute was uniformly set at 2,000 ppm, and the test solution was filtered under the transmembrane pressure of 3 atm. The concentration of the test solute in the filtrate was determined using a differential refractometer (Waters Co., R403). Solute rejection was then calculated to obtain the molecular weight cut-off of each membrane.

RESULTS AND DISCUSSIONS

Effects of DBSS

Hollow fiber was spun from the dope solution comprised of PS/NMP/PVP (= 15/70/15) at an air gap of 60 cm. The coagulation bath was filled with 0 to 15% DBSS aqueous solution, and the bore coagulant was fixed as pure water. Since the same bore coagulant was used, there is no difference in the structure of the inner surface. As shown in Figure 4, a skin layer was formed at the inner surface, and the fingerlike structure supported the skin layer. The fingerlike structure was suspended by the formation of sponge layer at the outer periphery when it contacted pure water, whereas, the fingerlike structure extended to the outer surface of the membrane, when

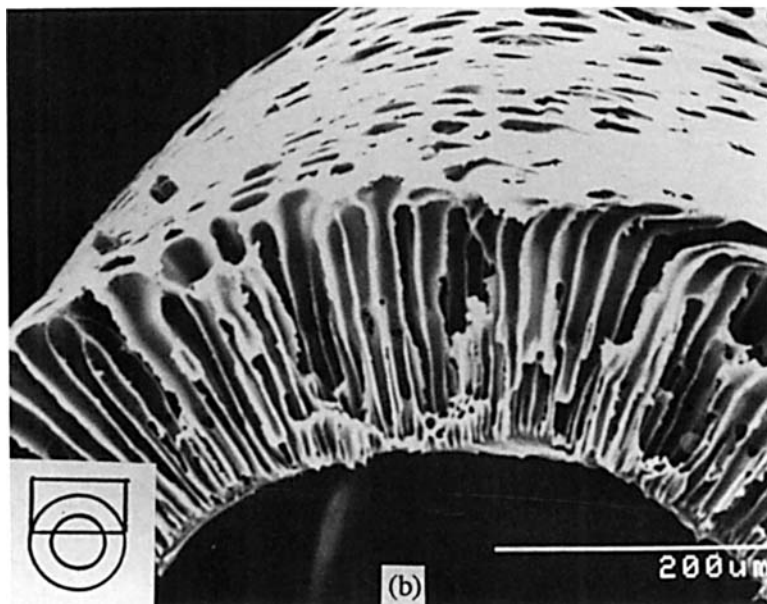
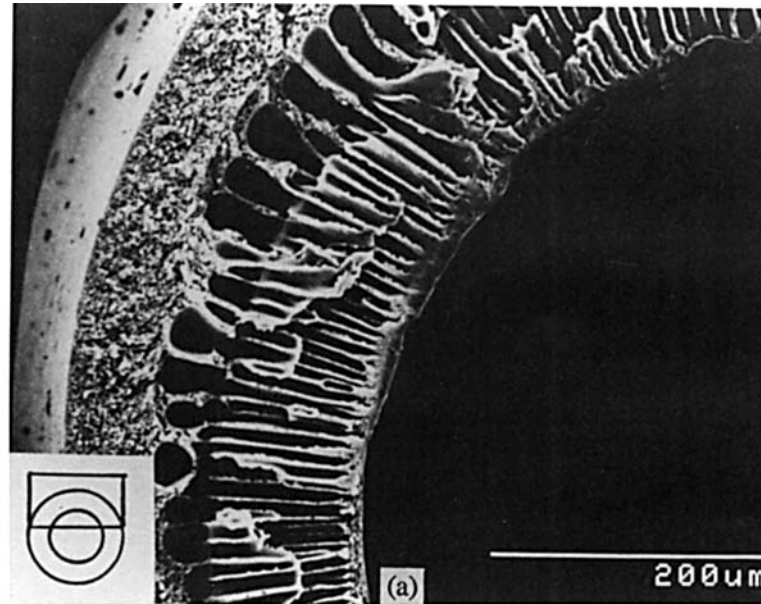


Figure 4 Cross sectional views of the hollow fiber membranes, coagulated in aqueous DBSS solutions of different compositions. (Dope solution: PS/NMP/PVP = 15/70/15, Bore coagulant: water, Outer coagulant: (a) pure water, (b) 5% DBSS aqueous solution).

5% DBSS aqueous solution was used as an outer coagulant.

The outer surface of the membrane, which contacted pure water (outer coagulant), showed a mi-

cro-porous structure [Fig. 5(a)], whereas those of the membranes that contacted DBSS aqueous solution had big pores [Figs. 5(b) and (c)]. These big pores corresponded to the extension of the fingerlike

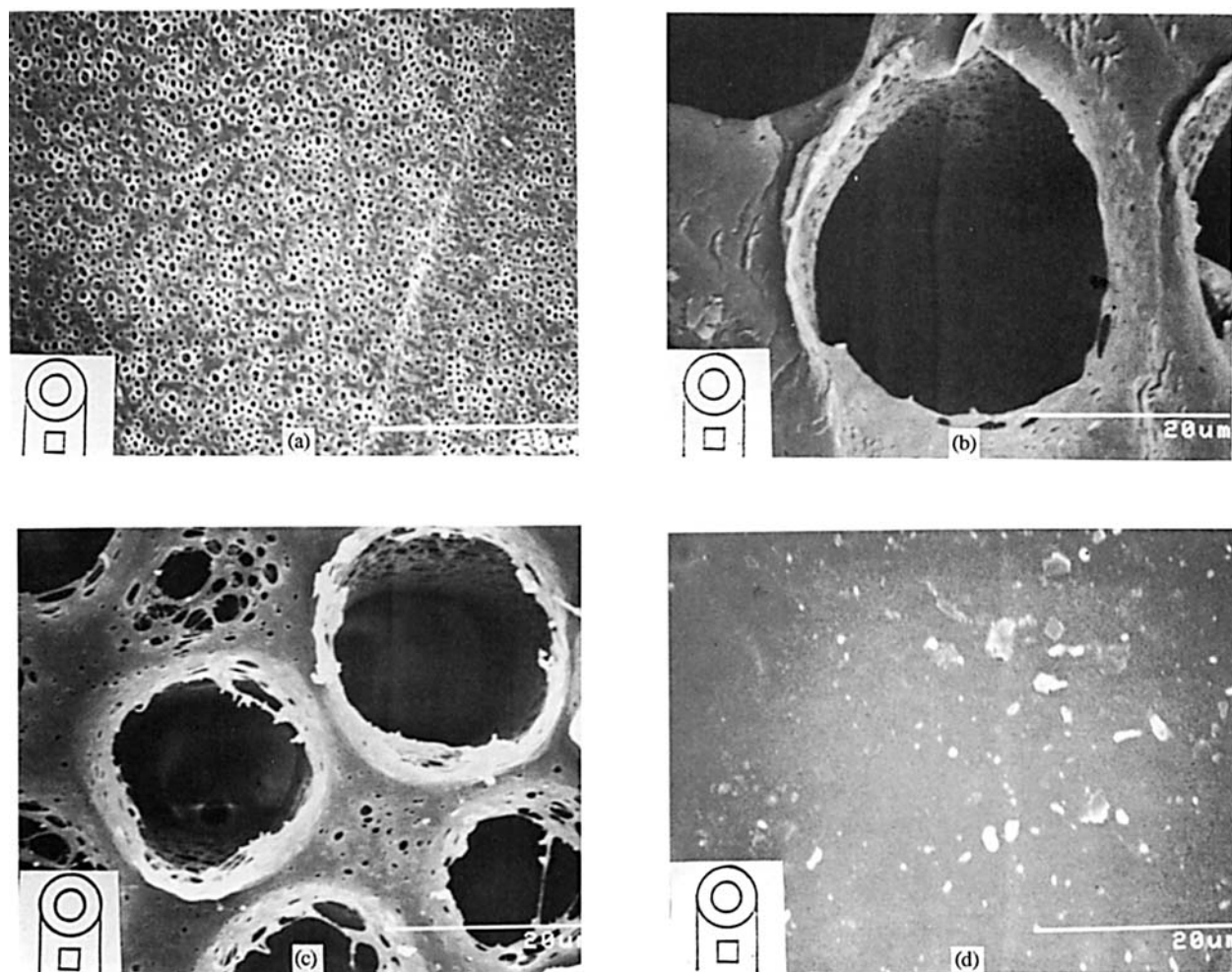


Figure 5 Outer surfaces of the hollow fiber membranes, coagulated in aqueous DBSS solutions of different compositions, as (a) 0%, (b) 5%, (c) 10%, (d) 15% (Dope solution: PS/NMP/PVP = 15/70/15, Bore coagulant: water).

structure to the outer surface, shown in Figure 4(b), and it can be easily observed that these big pores were formed by the agglomeration of neighboring tiny pores. Lots of tiny pores were formed in the initial stage via spinodal decomposition for every sample shown in Figure 5. The sample that contacted pure water retained the microporous structure, while the samples that contacted DBSS solution underwent the coarsening process via surface phenomena. Formation of the big pores was attributed to coarsening rather than nucleation and growth mechanism, since the presence of lots of tiny pores that were spread all over the sample proved that the sample underwent spinodal decomposition to make a lacy structure.

After the spinodal decomposition, each sample was driven to the equilibrium state of the system,

and the equilibrium sizes of the pores were determined by the surface tension, solution viscosity, and other physicochemical properties. The coarsening rate was also governed by these physicochemical properties, and some of the sample might not reach its equilibrium size before the solidification of the sample. Therefore, final pore size of each sample was determined by either equilibrium size or coarsening rate of the polymer-lean domain.^{20,21} Addition of DBSS to the outer coagulant altered the physicochemical properties of outer coagulant to result in changes in equilibrium size of the pores and coarsening rate. Another example of the pore size variation, by the addition of DBSS to the outer coagulant, is also illustrated in Figure 6 for the system, the dope solution of which was PS/NMP/PVP/DBSS (= 15/65/15/5).

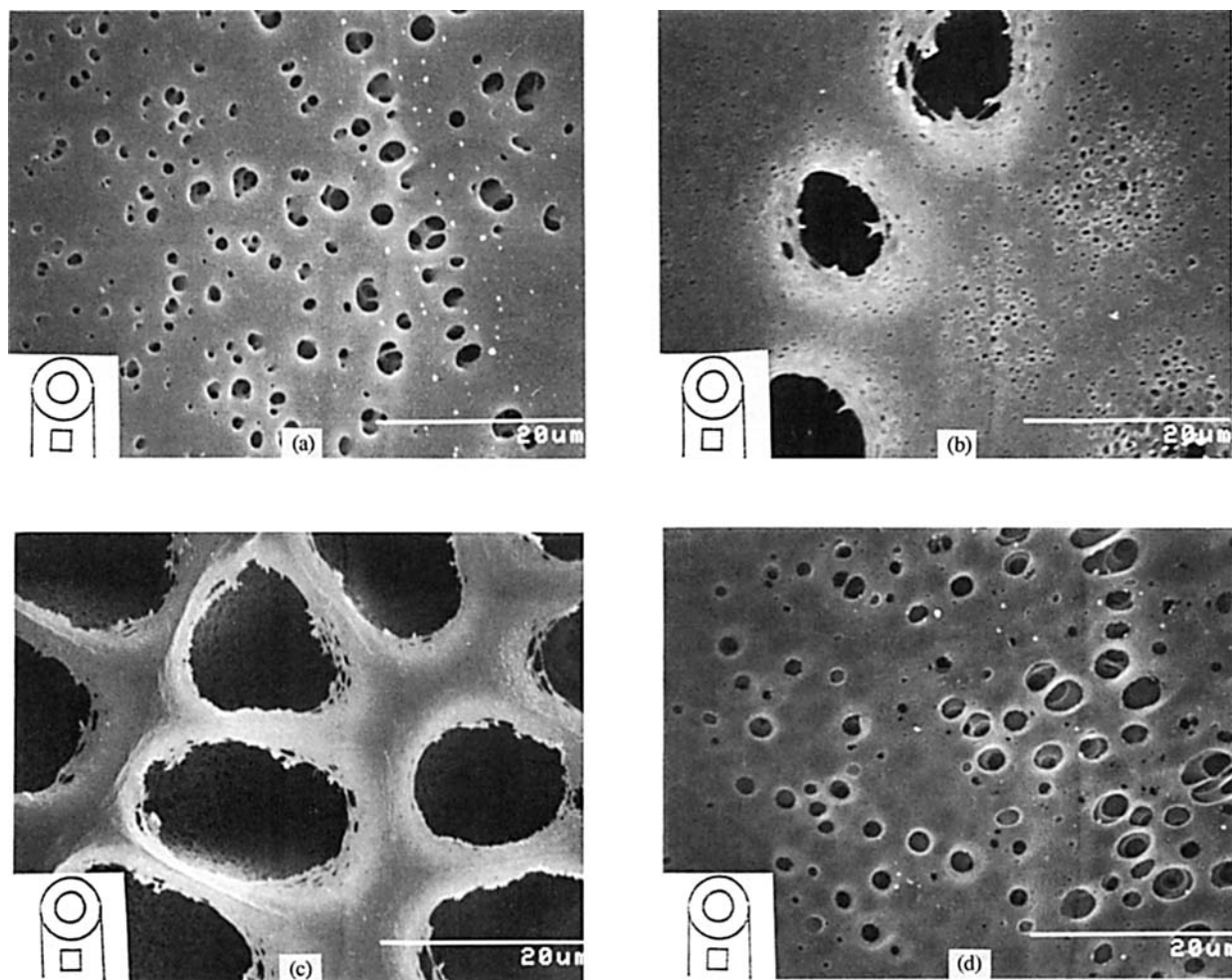


Figure 6 Outer surfaces of the hollow fiber membranes, coagulated in aqueous DBSS solutions of different compositions, as (a) 0%, (b) 5%, (c) 10%, (d) 15% (Dope solution: PS/NMP/PVP/DBSS = 15/65/15/5, Bore coagulant: water).

When pure water was used as an outer coagulant, the pore size of the sample shown in Figure 6(a) is much greater than that of the sample in Figure 5(a). The addition of DBSS to dope solution must have changed the physicochemical properties of the dope solution, and some of the DBSS has dissolved in the pure water. This should affect the coarsening characteristics of the sample, and the sample in Figure 6(a) seems to have undergone more coarsening to have a greater pore size than did the sample in Figure 5(a). Therefore, the addition of DBSS to the dope solution could also change the coarsening characteristics of the sample.

Maximum pore sizes were attained by the addition of DBSS to the outer coagulant at a DBSS concentration of around 5% for Figure 5 and 10% for Figure 6. Then, the pore size gradually decreased

with the increase of a DBSS amount in outer coagulant. An excess amount of DBSS in the outer coagulant might alter the physicochemical properties of outer coagulant to affect the coarsening characteristics. Since the transport properties of the membranes were directly related to the pore size of the membranes, pure water fluxes were measured to characterize the transport properties. Maximum pure water flux was obtained at 5% of DBSS in Figure 7 and 10% of DBSS in Figure 8, which exactly corresponded to the pore size change behaviors in Figures 5 and 6, respectively.

Quantitative analyses to support the explanations of the phase separation mechanisms, as stated above, have not yet been performed. The structural evidence for coarsening after spinodal decomposition, however, was clearly shown in the outer surface of

the membranes, and the pore size variation might be related to the coarsening. Measurements of various physicochemical properties at each incidence, and the visual tracing of the phase separation mechanism, are being conducted by our group for confirmation of these explanations.

Effect of PVP

In membrane preparation via the phase inversion method, several pore forming agents usually have been added to the dope solution to help pore formation. Typical pore forming agents are formamide for cellulose acetate membranes and PVP for polysulfone membranes.^{18,19,22} PVP was used in this study for the samples stated above, and membrane preparations were successfully performed. The effects of PVP on the membrane structure were examined by comparing the samples prepared from the dope solution containing PVP with those from the dope solution without PVP. The samples prepared without PVP (Fig. 9) had less porosity and smaller pore size than those prepared with PVP under the same conditions [Fig. 6(a) and (b)]. Therefore, it was partly revealed that PVP played an important role in the pore formation in these systems. The presence of DBSS in the outer coagulant also contributed to the increase of pore size in this case, since the sample

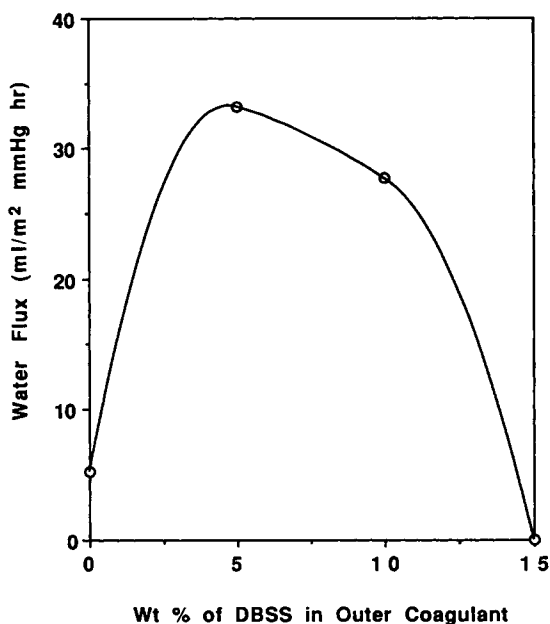


Figure 7 Water flux variation of the hollow fiber membranes, coagulated in aqueous DBSS solutions of different compositions. (Dope solution: PS/NMP/PVP = 15/70/15, Bore coagulant: water).

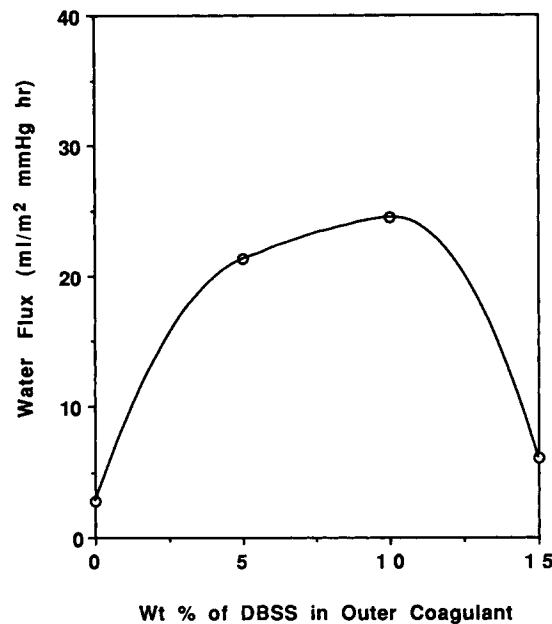


Figure 8 Water flux variation of the hollow fiber membranes, coagulated in aqueous DBSS solutions of different compositions. (Dope solution: PS/NMP/PVP/DBSS = 15/65/15/5, Bore coagulant: water).

coagulated in 5% DBSS aqueous solution had greater pore size than that in pure water, as shown in Figure 9.

Effect of Air Gap

The effect of air gap was also examined by measuring the water fluxes of the membranes prepared from the dope solution of PS/NMP/PVP = 15/70/15 at different air gaps. As shown in Figure 10, water flux increased with an increase of air gap, and showed a maximum at 60 cm of air gap. At greater air gaps, water flux decreased, and the membranes prepared above the air gap of 130 cm were fractured or showed leakage during the test. An increase of air gap usually resulted in skin formation at the outer surface of the membrane via evaporation of volatile solvent. Formation of skin lowers the transport properties of the membrane, since the dense layer works as a barrier.

However, the trend shown in Figure 10 did not correspond to this rationale. Since the vapor pressure of NMP was low, skin formation via solvent evaporation was not so significant as to be affected by air gaps below 60 cm. Decrease of water flux with air gaps over 60 cm seemed to be influenced by the skin formation. On the other hand, solvent/non-solvent interaction was more important below the

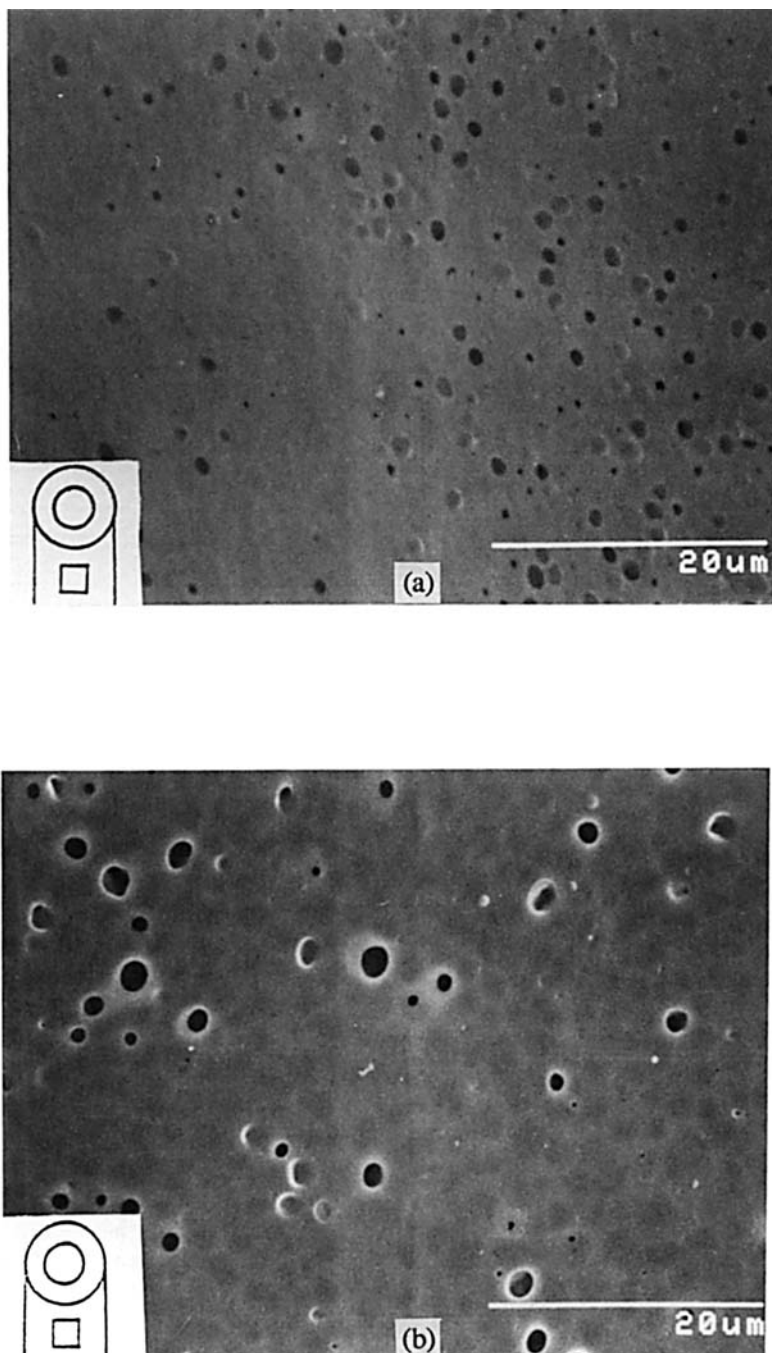


Figure 9 Outer surfaces of the hollow fiber membranes, prepared from dope solution of PS/NMP/DBSS = 18/77/5, with outer coagulant of (a) pure water and (b) 5% DBSS aqueous solution (Bore coagulant: water).

air gap of 60 cm, although the exact explanation for the interaction has not yet been provided.

Molecular Weight Cut-Off

An ultrafiltration membrane is usually characterized by its molecular weight cut-off. Among the many

samples prepared in this study, the membrane, which had been prepared from the dope solution of PS/NMP/PVP = 15/70/15, with air gap of 60 cm, and which was coagulated in 5% DBSS aqueous solution, was selected for the molecular weight cut-off test.

As shown in Figure 11, the membrane stated above began to reject the solute at a molecular weight of 7,000, and 90% of the solute was rejected at a molecular weight of 70,000. This is exactly the same as the molecular weight cut-off range of commercial hemofiltration membrane. Therefore, the membranes prepared in this study were suitable for hemofiltration, as well as for the general ultrafiltration processes. Since the molecular geometries of PEG and dextran are different from each other, the rejection plots in Figure 11 did not exactly coincide with each other.

CONCLUSIONS

The structure of the polysulfone membrane prepared in this study was formed via coarsening of the neighboring tiny pores, preformed via spinodal decomposition. The equilibrium size of the pore and the coarsening rate were determined by the physicochemical properties of dope solution and coagulant. The addition of DBSS to the outer coagulant altered the surface properties of the outer coagulant to change the pore size. The addition of DBSS to dope solution also altered the coarsening characteristics of the sample to result in greater pore size than the sample without it. PVP proved to act as a

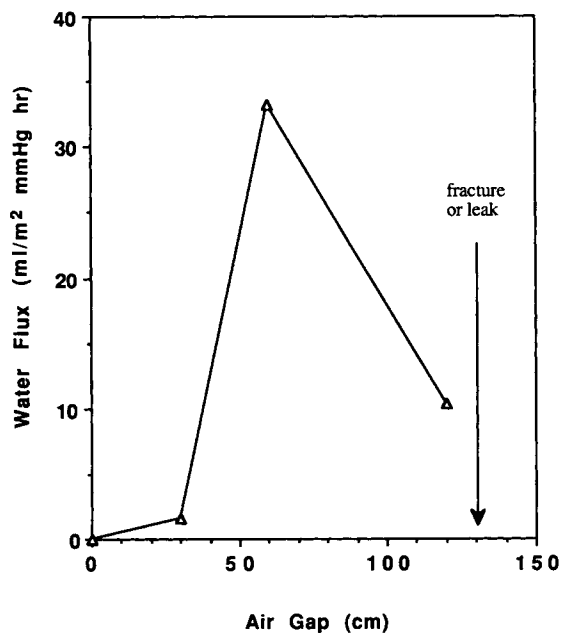


Figure 10 Effects of air gap on the water flux of the membrane from dope solution of PS/NMP/PVP/DBSS = 15/65/15/5 (Bore coagulant: water, Outer coagulant: 5% DBSS aqueous solution).

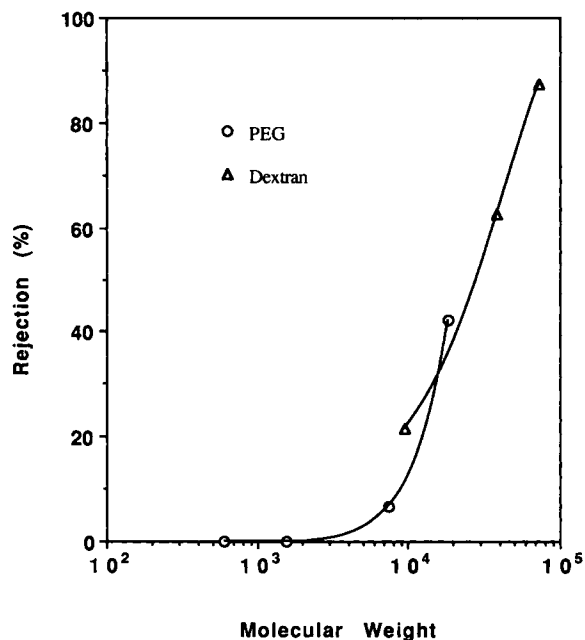


Figure 11 Solute rejections of PEG and dextrans of various molecular weights for the membrane from dope solution of PS/NMP/PVP/DBSS = 15/65/15/5 (Bore coagulant: water, Outer coagulant: 5% DBSS aqueous solution).

pore forming agent, which was important in attaining appreciable porosity and pore size of the membrane. Air gap also affected the membrane properties, and maximum water flux was obtained at 60 cm of air gap. In terms of the molecular weight cut-off characteristics, the membranes prepared in this study have application to the hemofiltration process. More quantitative analyses of the parameters are required for exact interpretation of the membrane formation mechanism.

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