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Factors Influencing the Production of Polyethersulfone Microfiltration Membranes by Immersion Phase Inversion Process

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ABSTRACT

Polyethersulfone microfiltration (MF) membranes can be produced from polyethersulfone/solvent/nonsolvent systems by the immersion phase inversion process in a water bath. When the casting solution composition is adjusted close to phase separation, a fast gelation in water occurs which hinders further polymer enrichment at the interface between polymer solution and water; an open-cell MF membrane structure is thus retained. Addition of a certain amount of a water-soluble polymer, polyvinylpyrrolidone, to the casting solution will further change the demixing rate and gelation rate of the casting solution in water. Such an addition improves the open-cell structure of the membranes. Besides dope composition, the performance of these MF membranes is also dependent on the casting conditions.

INTRODUCTION

Synthetic polymeric membranes used for separation applications are mainly made by phase inversion processes: the dry and dry/wet processes. In such phase inversion processes the membranes are formed by phase separation of a polymer solution upon contacting with water vapor (dry process) or a liquid precipitant (wet process) (1). The dry process for making microfiltration (MF) membranes was commercialized in the early

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1930s and this method is still used in commercial production of MF membranes and in research (2, 3). In the dry process MF, the membrane structure is formed by slow penetration of water vapor into the cast polymer film without a fast solvent outflow and a rapid increase in polymer concentration at the film surface. In the wet immersion process, however, the resulting membrane structure is influenced not only by a fast penetration of liquid precipitant but also by a fast outflow of solvent, which lead in many cases to the formation of a very dense and thin skin layer on top of the membrane, which is not suitable for microfiltration. This occurrence limits the use of the immersion phase inversion process for the production of MF membranes.

MF membranes have been successfully produced by means of the immersion phase inversion process (1, 4–7) in recent years. This has been achieved either by precipitation in a gelation bath containing solvent (1, 7) or by using a special dope composition (4, 5). Since a solvent-containing gelation bath reduces the outflow of solvent from the cast film and slows down the precipitation rate of the polymer, the mechanism involved in such immersion processes approaches that occurring in the dry process.

Immersion processes reported for making MF membranes from a few special casting solution compositions (4, 5) appear to be restricted to using certain polymers, solvents, and chemicals; hence, they do not provide a general method for MF membrane preparation by gelation in a water bath.

In this paper an immersion phase inversion process for making MF membranes is described in which polyethersulfone MF membranes are made by using a water gelation bath without the addition of solvent to the bath. The influence of casting conditions on the performance of the resulting membranes will be discussed. The way by which dope composition can be changed in order to get MF membranes with large pores provides a general approach for formulating casting solutions for the production of MF membranes by gelation in a water bath.

EXPERIMENTAL

Polymer solutions were prepared containing 12 or 15 wt% polyethersulfone (PES) using solvents with moderate solvent power and nonsolvents at ambient temperature. PES (Vitrex 4800) was purchased from I.C.I. The solvents used were dimethylacetamide (DMAc) of c.p. grade and dimethylformamide (DMF) of G.R. grade; both were supplied by Merck. The nonsolvents in the casting solutions were ethanol (EtOH) of G.R. grade, diethylene glycol (DegOH) of c.p. grade, and ethylene glycol (EgOH) of A.R. grade. Water-soluble polyvinylpyrrolidone (PVP) from

Sigma with a molecular weight of 10,000 dalton was also used as an additive in some experiments.

Prior to the preparation of the polymer solution, PES was dried for 3 hours at 150°C according to a recommendation from the supplier. The casting solution consisted of PES, a nonsolvent, a solvent or a solvent mixture, and sometimes the PVP additive. They were handcast onto glass plates cleaned and dried by acetone in a membrane casting room with a controlled relative humidity: ~55%. Generally, cast films with a film thickness of 150 μm (unless otherwise specified) were immersed into a deionized water bath at a controlled water bath temperature as quickly as possible to avoid exposure to air. In a few special cases the cast films were allowed to contact with air for a given time before they were put into the water bath. Membranes were stored in deionized water for further characterization.

Membranes were characterized in terms of their water flux by permeation measurement and their biggest pore size by bubble point measurement (8). For permeation measurements the wet membrane was installed in a Sartorius filter holder (Sartorius GmbH, Germany) with a 200-mL capacity and a 12.5-cm^2 filtration area. The flow rate P of deionized water through the membrane was measured under an operating pressure of 1 bar (gauge). For bubble point measurements, the wet membrane was mounted inside a stainless steel cell. Compressed air was introduced into the cell. The air flow rates through the membrane at different air pressures were registered either by displacement of water from a measuring cylinder or by flowmeters. The biggest pore size of the membrane, d_{max}, was calculated using air pressure at which a sharp rise in the air flow (8) through the membrane occurred. Depending on the permeability of the membranes, the bubble point measurements were carried out with the membranes taken from storage or after having been flushed with 50 mL isopropanol.

The membrane structure was examined from scanning electron photomicrographs (SEM) taken with a Jeol JSM-T330A scanning electron microscope.

RESULTS AND DISCUSSION

Influence of Dope Composition

The mechanism of the immersion phase inversion process for flat MF membrane preparation can be described briefly as follows.

After the film cast on a glass plate is immersed in a precipitation bath, liquid–liquid phase separation occurs due to changes in local composition, such as depletion of the solvent, penetration of the precipitant, and an increase in polymer concentration at the film surface.

This liquid–liquid phase separation forms droplets, giving rise to an interdispersed phase (9). Fine particles (nodules or nodular aggregates), which already exist or are later created in the cast film by nucleation before and after the liquid–liquid phase separation process, disperse on the droplets and grow progressively to larger particle aggregates (super nodular aggregates). They finally transform the polymer solution into a gel consisting of a low-molecular phase and a polymer network phase with a cell structure. Contraction of the cells tears off the cell walls between adjacent cells to yield the final open-cell structure in a MF membrane (10).

The art of MF membrane production by immersion phase inversion process lies, therefore, on a sensible control of the aggregate size in a polymer solution and on the gelation rate of this polymer solution in a particular precipitation bath. In a precipitation bath containing solvent, this polymer gelation rate is moderately fast, therefore the starting aggregate size in this polymer is relatively small. When a strong precipitant like water is used, the incipient aggregate size in a polymer solution should be adjusted by the addition of a nonsolvent, such that gelation of this polymer solution takes place immediately upon contact with water.

In Fig. 1 the results of permeation and bubble point measurements are presented for PES membranes prepared from a 15 wt% polymer solution in DMAc by the immersion technique in a plain water bath at 25°C. The nonsolvents tested were EtOH, EgOH, and DegOH at a 0.3 weight ratio of nonsolvent (NS) to solvent (S) (W_{NS}/W_S).

Membranes prepared using EgOH as the nonsolvent yielded the highest permeability and the biggest pore size. This difference in performance between membranes prepared from the PES/EgOH/DMAc and the PES/DegOH/DMAc systems is understandable. A separate test showed that the maximum weight ratio $(W_{NS}/W_S)_{max}$ without causing precipitation in the casting solution was 0.35 for PES/EgOH/DMAc and 0.7 for PES/DegOH/DMAc. At the same nonsolvent/solvent ratio, aggregates in the PES/EgOH/DMAc system (and thus the pore size of membranes made from this system) are therefore bigger than those in the PES/DegOH/DMAc system. For these PES/EtOH/DMAc and PES/EgOH/DMAc systems at the same value of $(W_{NS}/W_S)_{max}$, the difference in densities of EtOH and EgOH would cause polymer precipitation to occur at different rates, and a denser surface layer will appear in membranes made from the PES/EtOH/DMAc system.

Figure 2 compares the performance of PES membranes prepared in a water bath (25°C) using PES/EgOH/DMF-DMAc and PES/EgOH/DMAc

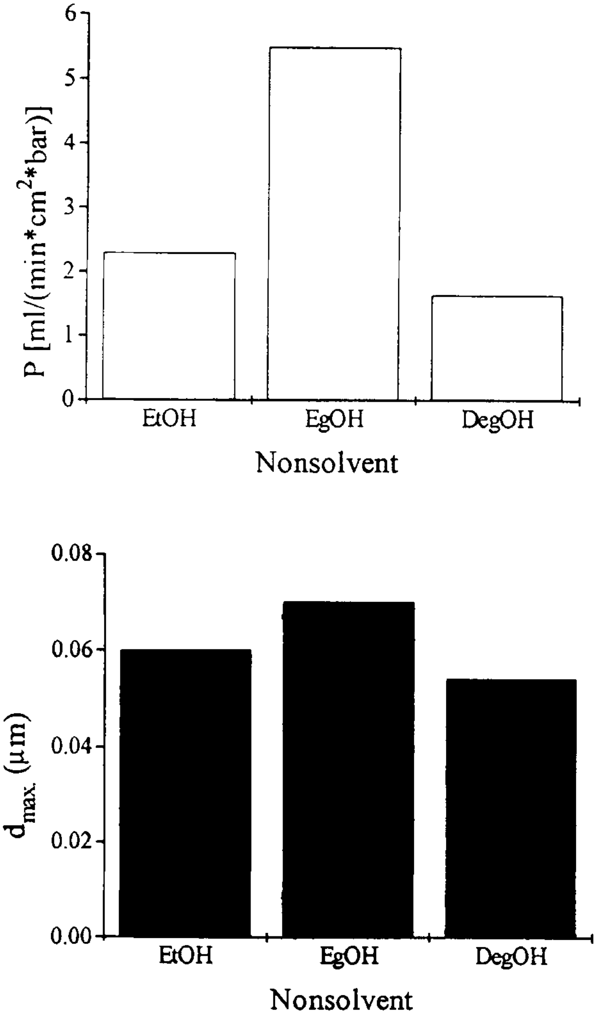

FIG. 1 Influence of nonsolvent on permeability P and the biggest pore size d_{max} of PES membranes gelled in a water bath at 25°C. Casting solution: 15 wt% PES in solvent DMAc; W_{NS}/W_S: 0.3.

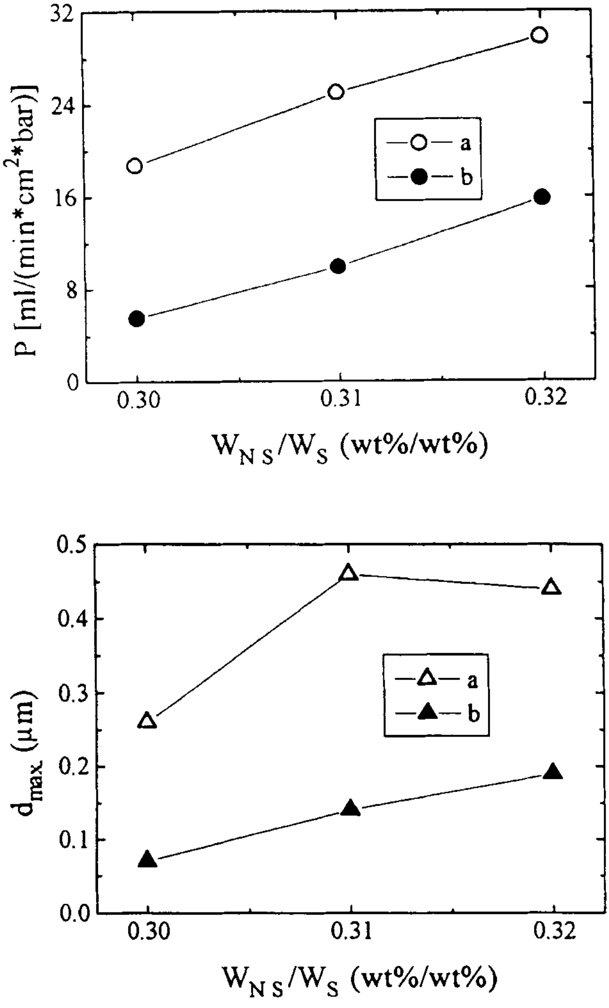

FIG. 2 Effect of W_{NS}/W_S in the casting solutions on permeability P and biggest pore size d_{max} of PES membranes gelled in water bath at 25°C. Casting solutions: a) 15 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc. b) 15 wt% PES; NS: EgOH; S: DMAc.

systems at various W_{NS}/W_S ratios. In both systems an increase in W_{NS}/W_S from 0.3 to 0.32 increased both P and d_{max} significantly. This is understandable on the basis that an increase in the W_{NS}/W_S ratio tends to increase the size of the polymer aggregates in the film casting solution, leading to the formation of bigger aggregate pores on the membrane surface. Similar results have been reported before in the development of ultrafiltration (UF) membranes (11). The effect of a 20:80 DMF:DMAc solvent mixture in the film casting solution on the P and d_{max} of the resulting membranes is particularly significant. Figure 2 shows that at W_{NS}/W_S values of 0.3 and 0.32, P and d_{max} of the membranes from the PES/EgOH/DMF-DMAc system were over 2 to 3 times, respectively, compared to those of membranes from the PES/EgOH/DMAc system. This is again understandable on the basis that the size of the polymer aggregate in the PES/EgOH/DMF-DMAc system is much bigger than that in the PES/EgOH/DMAc system, which is consistent with the lower solubility of PES in DMF, indicated by a $(W_{NS}/W_S)_{max}$ value of 0.1 for EgOH in DMF.

The influence of solvent composition in the polymer solution on membrane performance observed in Fig. 2 is further confirmed in Fig. 3. A sizable increase in membrane permeability was achieved by increasing the weight ratio of DMF to DMAc in the casting dope.

Figure 4 illustrates the effect of inclusion of PVP in the film casting solution on P and d_{max}. Two casting solutions were used, one with DMAc as solvent and the other with DMF–DMAc (20/80) as a mixed solvent. In both cases the PES concentration was 12 wt% and W_{NS}/W_S was 0.3; the gelation medium was pure water at 25°C. With the addition of PVP the viscosity of the film casting solution increased.

Figure 4 shows that there exists an optimal PVP content beyond which P and d_{max} of PES membranes will decline. Since the addition of nonsolvent or additive to a polymer solution will increase the polymer aggregate size, an increase in permeability and pore size in the membranes is expected upon the addition of PVP. The decline in P and d_{max} in membranes prepared from both systems with a PVP content of 20 wt% may be due to a delay in the demixing of the polymer solution. A delayed demixing hinders the growth of existing aggregates and promotes nucleation in the polymer solution upon immersion (12), which will lead to the formation of smaller pores.

Figure 4 also shows that with PVP at 2 wt%, a lower PES concentration (12 wt%) yielded membranes with much bigger pores and much higher permeability than membranes made from a similar system of higher PES concentration at 15 wt% (Fig. 2). However, a minimum polymer concentration in the film casting solution is obviously necessary so that the result-

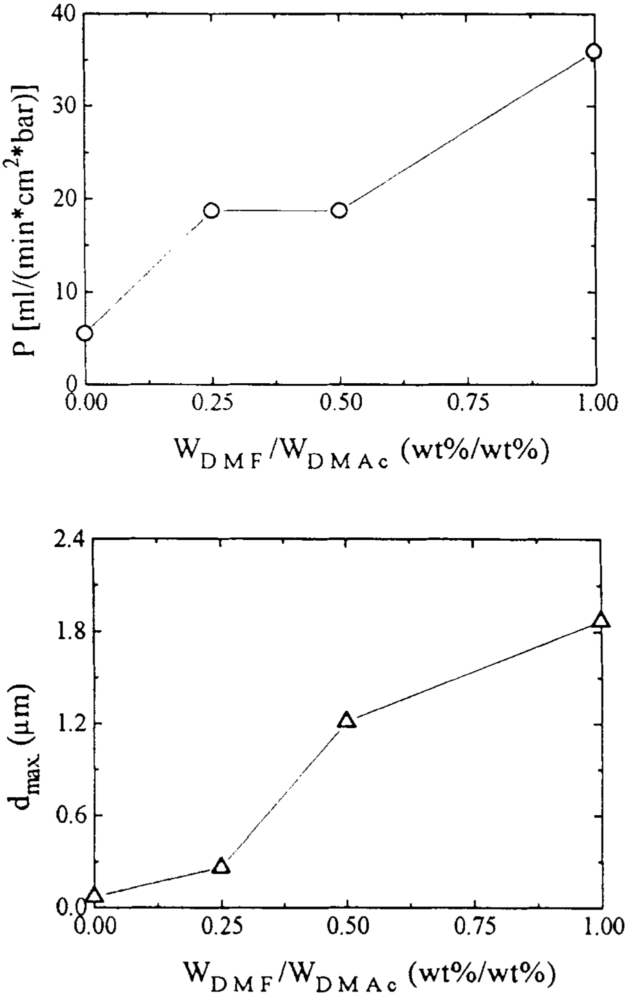

FIG. 3 Effect of solvent composition in the polymer solution on permeability P and biggest pore size d_{max} of PES membranes gelled in water bath at 25°C. Casting solution: 15 wt% PES; NS: EtOH; S: DMF + DMAc; W_{NS}/W_S: 0.3.

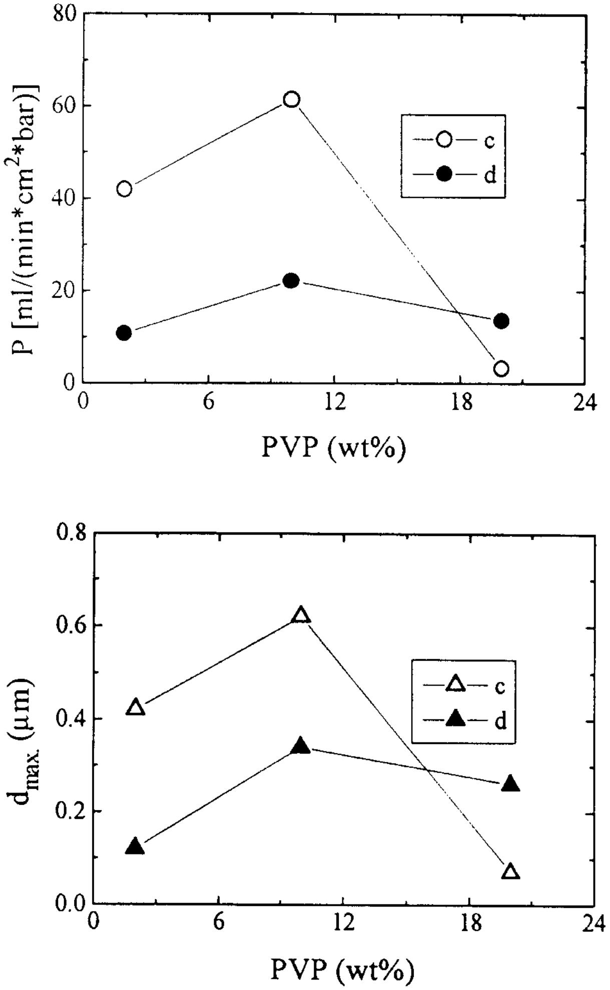

FIG. 4 Effect of PVP content on permeability P and biggest pore size d_{max} of PES membranes gelled in water bath at 25°C. Casting solutions: c) 12 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc; W_{NS}/W_S: 0.3. d) 12 wt% PES; NS: EgOH; S: DMAc; W_{NS}/W_S: 0.3.

ing membranes can withstand the operating pressure used in microfiltration.

Influence of Casting Conditions

Figure 5 shows the influence of gelation water bath temperature on the performance of PES membranes.

When temperature of the gelation bath was increased from 0 to 25°C and then to 45°C, the permeability (and the biggest pore size) of the resulting PES membranes was increased by 304.2% (188.9%) and 408.9% (300%), respectively. An increase in mass transfer between the cast film and the precipitant (water) at higher water bath temperature might be the reason for a fast demixing which led to formation of larger pores in the membrane.

Generally, exposure of a cast film to air with relative humidity of 55% will change the polymer aggregate size in the cast film and gelation characteristic of the film. The closer the cast film composition is to phase separation, the more the polymer aggregates will be affected. Polymer solution composition and cast film exposure time will affect the performance of the membrane made by the immersion phase inversion process.

Figure 6 shows that when the exposure time of a cast film increased from 0 to 15 seconds, a 72.4% increase in permeability was achieved. It is interesting to note that $d_{\max}$ remained unchanged in the 0 to 15 seconds exposure time. This increase in P therefore must have come from the bigger number of pores formed after a 15-second exposure to air. A further increase in exposure time from 15 to 30 seconds, however, caused a steep reduction in P and $d_{\max}$ in the membranes. Too long an exposure allowed polymer aggregates in the top layer to fuse with each other, resulting in fewer pores.

Thicker cast films are expected to yield membranes with a thicker top layer, which in turn poses higher resistance to fluid flow through the membranes. Figure 7 illustrates the effect of cast film thickness on the P and $d_{\max}$.

Figure 7 shows that permeability of PES membranes decreased drastically when the thickness of the cast film was increased from 150 to 200 μm, which reflects the combined effect of thicker membrane top layer and fewer and smaller pores. Mass transport of polymer from bulk of a thicker cast film is always higher than from the bulk of a thin cast film. At the incipient state of membrane formation, this supply of polymer from bulk toward the polymer/water interface keeps the polymer concentration at the membrane top layer high, which encourages formation of smaller pores.

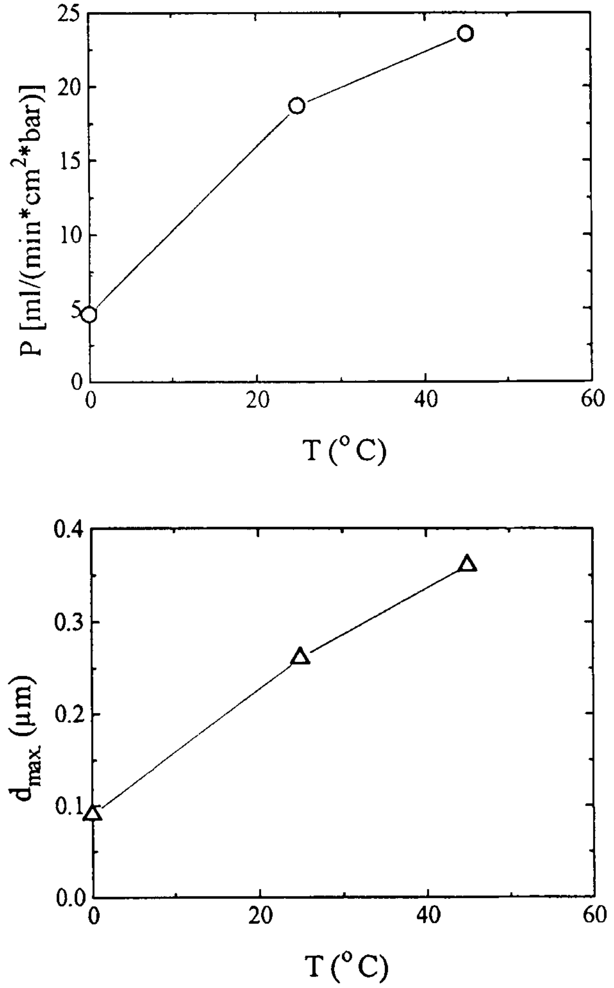

FIG. 5 Influence of gelation water bath temperature on permeability P and biggest pore size d_{max} of PES membranes. Casting solution: 15 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc; W_{NS}/W_S: 0.3.

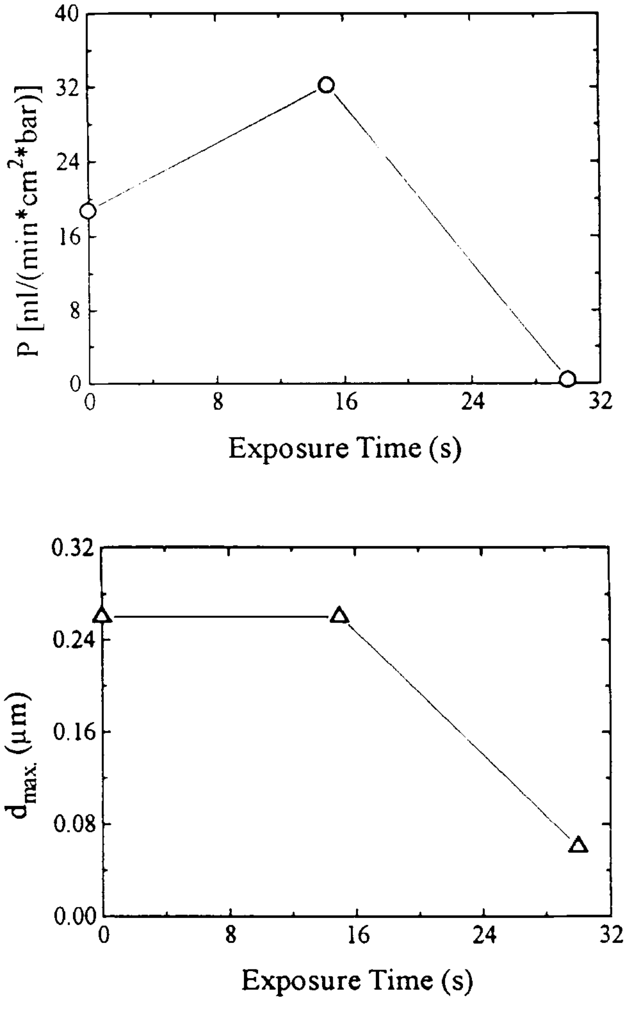

FIG. 6 Influence of exposure time on permeability P and biggest pore size d_{max} of PES membranes gelled in water at 25°C. Casting solution: 15 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc; W_{NS}/W_S: 0.3.

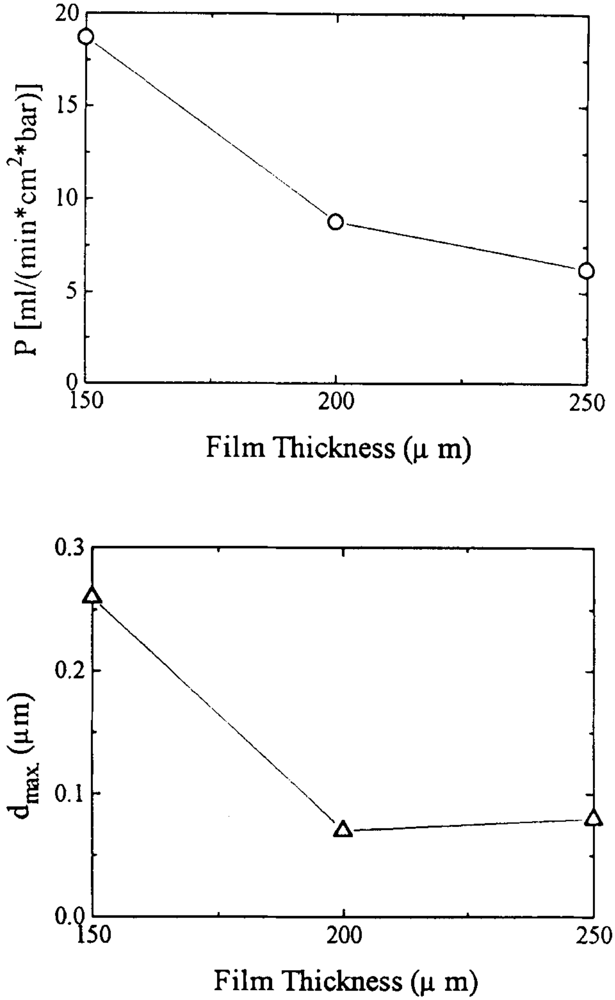

FIG. 7 Influence of cast film thickness on permeability P and biggest pore size d_{max} of PES membranes gelled in water at 25°C. Casting solution: 15 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc; W_{NS}/W_S: 0.3.

SEM Examination

In Fig. 8, SEM of the cross section of a PES membrane (8a) shows a increasing porosity from the top layer (facing toward water side) to the sublayer (facing toward the glass plate). Figure 8(b) shows a closer examination of the top layer in Fig. 8(a). There is a region of relatively larger pores, an asymmetricity other than the conventional type. Further SEM examinations on other PES membranes show that such a layer exists in all membranes prepared from DMF–DMAc solvent mixtures and in membranes prepared using DMAc as solvent with a 0.32 weight ratio of EgOH to solvent (Fig. 2) without exposure to air before gelation in the water bath. The relatively poor solvent power in DMF–DMAc solvent mixtures and in DMAc solvent with a large EgOH/solvent ratio can cause a fast demixing and gelation of PES at the water/polymer solution interface before the local polymer concentration in this "porous region" can be increased by a mass transfer of polymer from the bulk.

SEM in Fig. 9 show cross sections of membranes prepared using the same polymer solution and procedure as those in Fig. 8 except that the cast film was exposed to air for 30 seconds before gelation in a water bath at 25°C. Photomicrograph 9(a) shows an overall porous cross section with big cells. These cells developed after the polymer solution at the air/cast film interface had already phase separated and gelled. Due to the presence of this gelled polymer surface, phase separation of the polymer in the bulk phase occurred at a much slower rate compared to the intensive mass transfer of solvent and water which occurred during the membrane formation without the 30-seconds exposure to air. The cells were thus less contracted and the cell walls were not torn off (Fig. 9b). The closed cell structure in these photomicrographs confirms the low permeability of these membranes (see Fig. 6).

The effect of PVP on PES membrane structure is shown in Fig. 10. SEM 10(a) and 10(b) show cross sections of PES membranes with a classical asymmetric structure, showing a gradual increase of the porosity from the top layer to the sublayer. In comparison with the photomicrograph 8(b), the top-layer region shown in the photomicrograph 10(b) does not possess any top-layer section with a larger porosity than that of the following layers. In comparison to using EgOH as nonsolvent, the addition of PVP to a PES polymer solution with DMAc as solvent changes the demixing and gelation characteristic of the casting solution.

Strong interactions between PVP and PES were reported by Lafrenière et al. (13) and Boom et al. (12) in the PES/*N*-methylpyrrolidone/PVP systems for producing PES UF membranes by immersion phase inversion process. In one case the permeation rate of the PES UF membranes was

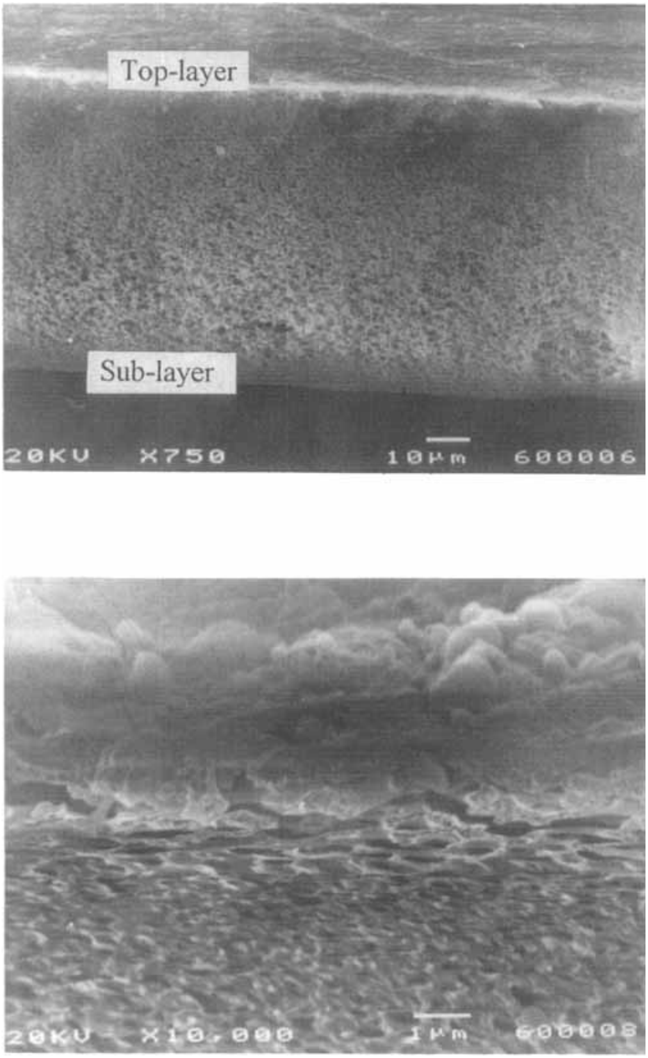

FIG. 8 SEM of PES membrane cross section (a) and top-layer region (b). Casting solution: 15 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc; W_{NS}/W_S: 0.3. Casting procedure: Gelled in water at 25°C.

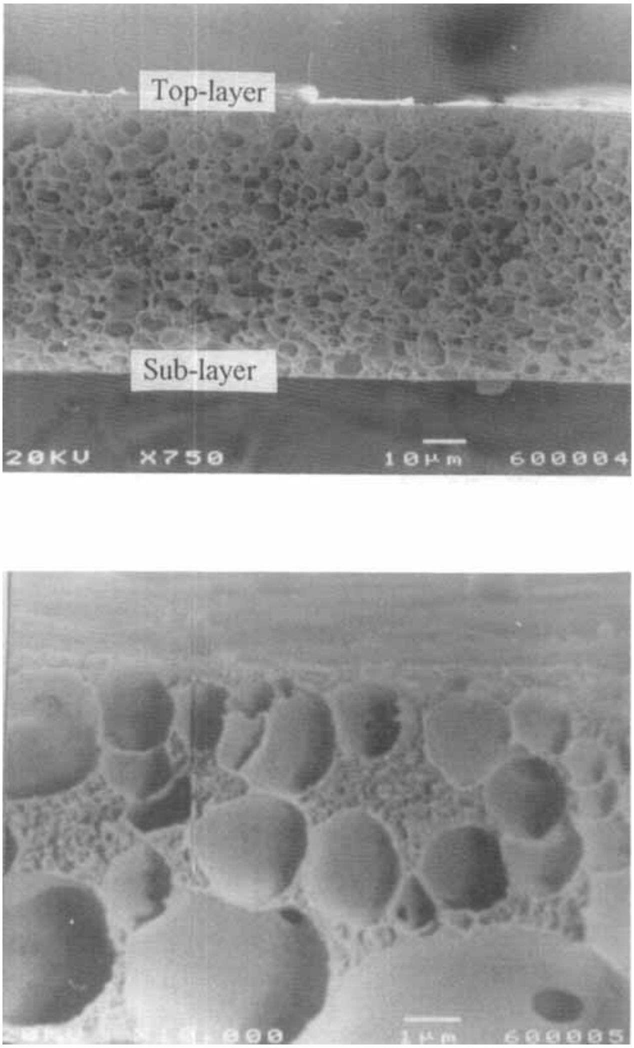

FIG. 9 SEM of PES membrane cross section (a) and top-layer region (b). Casting solution: 15 wt% PES; NS: EgOH; S: 20 wt% DMF + 80 wt% DMAc; W_{NS}/W_S: 0.3. Casting procedure: 30 seconds exposure time to air, gelled in water at 25°C.

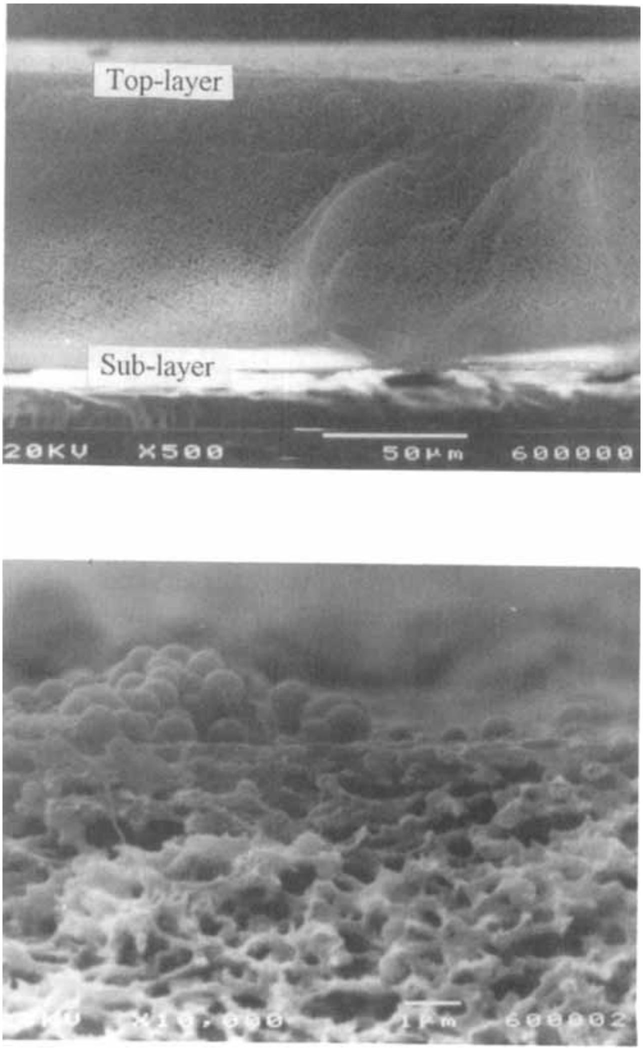

FIG. 10 SEM of PES membrane cross section (a) and top-layer region (b). Casting solution: 12 wt% PES: 20 wt% PVP; NS: EgOH: S: DMAc: W_{NS}/W_S: 0.3. Casting procedure: Gelled in water at 25°C.

increased by an appropriate choice of PES/PVP weight ratio (13), while in another case macrovoid development in the sublayer of their PES UF membranes was successfully suppressed by addition of a certain amount of PVP into the PES casting solutions (12).

Boom et al. (12) explained that the influence of PVP in a PES casting solution in an immersion phase inversion process takes place in two time scales. In the initial short time scale, PVP and PES molecules in the casting solution move with respect to each other slowly, and in the long time scale they move relatively fast. Nucleus growth leads eventually to a macrovoid by a delay of demixing of polymer molecules surrounding a nucleus. But creation of nuclei instead of nucleus growth is predominant in the initial short time scale.

For PES membranes shown in Fig. 10 this two time scale model is also applicable. Addition of 20 wt% PVP to the PES casting solution increases the polymer aggregate size and reduces the gelation rate of PES upon immersion due to interaction between PES and PVP. When these aggregates start to gel, part of the DMAc/EgOH mixture in the cast film had already been replaced by the precipitant (water) by virtue of its relatively fast mass transfer. Increase in nonsolvent concentration in the bulk film induced larger aggregates to form, which in turn enhanced the contraction of cell walls in the gelation stage and created a more open cell structure in the membrane sublayer. Other nonsolvents confer a similar effect on PES membrane structure, as shown in Fig. 8. The membrane top-layer structure in Fig. 8 was created by the fast demixing (fast gelation) of PES in a poor solvent with a high EgOH to solvent ratio. This fast gelation of PES at the cast film/water interface resulted in a top layer with fewer open cells, which slowed down mass exchange across the cast film. A substructure in the PES membrane under this top layer thus developed in an environment where influx of water and outflow of the solvent/EgOH mixture were slow.

CONCLUSION

Polyethersulfone (PES) MF membranes with a permeability of 5.49–61.40 mL/(min·cm^2·bar) and a biggest pore size of 0.07–1.87 μm can be produced by an immersion phase inversion process from PES/solvent/nonsolvent systems in a water bath when the dope composition of the casting solution is appropriately adjusted. Use of the DMF–DMAc solvent mixture for the PES solution preparation and addition of EgOH into the casting solution increase polymer aggregate size in the solution, which causes a fast gelation upon immersion into water bath. This fast gelation of PES casting solution hinders further polymer enrichment at the interface between the cast film and water, which helps to retain an open-cell MF membrane structure in the membrane.

PES MF membranes produced from a casting solution of 12 wt% PES and a given weight ratio of EgOH to solvent possess high water permeability and bigger pore sizes in comparison to membranes made from a casting solution of 15 wt% PES. Addition of a certain amount of water-soluble polymer PVP to a 12 wt% PES casting solution will change the demixing characteristic of the solution and enable the PES MF membrane to form an asymmetric open-cell structure.

For PES membranes prepared from casting solutions with a composition close to phase separation, permeability and pore size of these membranes are strongly influenced by the casting conditions, such as gelation water bath temperature, exposure time to air, and thickness of the cast film. Generally, a decrease in the water bath temperature and an increase in cast film thickness will reduce permeability and pore size of the membrane. A short exposure of the cast film to air at 55% relative humidity will increase the membrane flux, while a long exposure will cause pregelation of the cast film which will reduce the intensive mass transfer between the cast film and water in the water bath to form a membrane structure with closed cells.

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