Polysulfone Membranes. III. Performance Evaluation of Polyethersulfone—PVP Membranes

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ABSTRACT

The performance of membranes produced from casting solutions consisting of polyethersulfone (PES), poly-(N-vinyl-pyrrolidone) (PVP), and N-methyl-2-pyrrolidinone (NMP) were systematically studied. Zero-shear casting solution viscosities for these polymer solutions were determined as a function of PES and PVP concentrations. Ultrafiltration membranes were then cast using the phase inversion technique and characterized by separation experiments using polyethylene glycols of various molecular weights as test solutes. A pore flow model was fitted to the resulting separation data to provide estimates of the average pore radius and membrane porosity. These parameters were used to compare laboratory results for this membrane casting solution system with performance data for commercially available polyethersulfone membranes.

INTRODUCTION

Polysulfones constitute a family of engineering plastics containing a sulfone group in the monomer unit. Bisphenol-A polysulfone (Udel) is one commonly available material used in the manufacture of ultrafiltration membranes. Polyethersulfone (PES) is another member of the polysulfone family that is commonly used for ultrafiltration membrane manufacture. PES has superior physical and chemical properties compared to Bisphenol-A polysulfones (1). As a result, this polymeric material is considered to be an ideal candidate for membrane separations that involve extreme process conditions.

In order to be a suitable candidate for use as a membrane material, a polymer must possess good film-forming properties. The resulting film must have some degree of permeability as well as allowing preferential transport of selected components of a solution. In the case of PES, membrane performance characteristics have been reported for various solvents, casting solution compositions, and casting conditions (2, 3). Additives such as poly-(N-vinyl-pyrrolidone) (PVP) are frequently included in the casting formulation to alter the behavior of the casting solution and, as a consequence, the membrane structure. This type of approach has been described by Lafrenière et al. (4) and Miyano et al. (5, 6). In both studies it was concluded that the membrane pore size and pore size distribution were related to the casting solution composition.

Membrane design implies the ability to control the separation behavior as well as the flux of a membrane. Optimizing membrane performance involves an inevitable trade-off between separation and permeation rate. This compromise can be expressed quantitatively by two membrane structural parameters obtained from solute separation experiments. The average pore radius is obtained from fitting a steric transport model to solute separation results. The ratio of number of pores per unit membrane area to pore length describes the membrane permeability. Performance data for commercial polysulfone membranes (7) and Bisphenol-A polysulfone/PVP membranes (8) was discussed in previous papers.

In this paper, previous work on characterizing the performance of polysulfone membranes is extended to the PES:PVP:N-methyl-2-pyrrolidinone (NMP) polymer:additive:solvent system. Zero-shear casting solution viscosities and membrane structural parameters are reported as a function of casting solution composition. Based on these results, the performance of laboratory-cast PES:PVP:NMP membranes is compared with performance data for commercially available polyethersulfone membranes.

THEORY

A pore model was used to describe solute transport through the membrane. The detailed derivation of the transport equation can be found elsewhere (9, 10). The solute separation (f) as a function of the pore Peclet number (Pe) is given by

$$f = 1 - \frac{\chi}{1 - e^{-Pe}(1 - \chi)} \tag{1}$$

The value of Pe is indicative of the ratio of convective transport to diffusive transport. Parameters describing the steric effects on restricted convective transport (χ) and the restricted diffusive effects (ξ) are incorporated into the definition of Pe so that

$$Pe = \frac{\chi}{\xi D_\infty} \left[\frac{r_p^2 \Delta P}{8\eta} \right] \tag{2}$$

where D_∞ is the diffusivity of the solute in the bulk solution, η is the viscosity of the solvent (in this case, water), and ΔP is the pressure differential across the membrane. Transport parameters χ and ξ are functions of λ, the ratio of solute radius to pore radius. Both parameters have been evaluated numerically based on a center-line approximation (9).

The permeability of a membrane for a given pore size can be obtained by measuring the flux of water or pure water permeation rate (PWP). The Hagen–Poisueille equation for volumetric flow rate (Q) through parallel cylindrical pores of radius r_p can be written as

$$Q = \frac{n \pi \Delta P r_p^4}{8\eta \Delta x} \tag{3}$$

where n is the number of pores and Δx is the effective pore length. For a membrane of area A, the ratio of the number of pores per unit area to the effective pore length is obtained by substituting the pure water permeation rate (PWP) for Q in Eq. (3), yielding

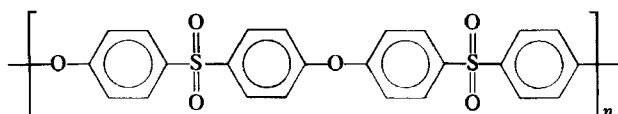$$\frac{n}{A \Delta x} = \frac{8\eta}{\pi \Delta P r_p^4} \frac{PWP}{A} \tag{4}$$

r_p and $n/A\Delta x$, determined by using Eqs. (1) and (4), are the minimum structural parameters necessary for direct comparison of membrane performance. The average pore radius determines the separating characteristics of a membrane. Higher separations are achieved with smaller pore

radius membranes for a given solute molecule. The parameter $n/A \, \Delta x$ describes the overall permeability of the membrane for a specific pore radius. This ratio includes the combined effects of the number of pores per unit area, the pore length, as well as the tortuosity of the pore. A larger value for this parameter indicates higher water flux through the membrane and implies either greater porosity (large n) or reduced pore length (small Δx), indicating less resistance to permeation through the porous membrane.

EXPERIMENTAL

Membrane Casting

The chemical structure for polyethersulfone (Victrex, 4100P) is shown below.

This polymer was obtained from ICI (Welwyn Garden City, UK). Poly-(N-vinyl-pyrrolidone) with a nominal average molecular weight of 10,000 daltons (PVP-10K) was supplied by Sigma (St. Louis, Missouri, USA). Reagent grade N-methyl-2-pyrrolidinone was obtained from Aldrich (Milwaukee, Wisconsin, USA) and was used without further purification. Casting solutions containing varying weight percentages of PES:PVP:NMP were prepared. Membranes were hand cast onto a spun bonded polyester backing material manufactured by Filtration Sciences Corporation (Mt. Holly Springs, Pennsylvania, USA) using a casting blade with a clearance of 0.01 mm. The nascent membranes were gelled by immersion in deionized ice water (4°C).

Viscosity Measurements

Casting solution viscosities were measured with a Haake Roto-Visco rotational viscometer (Dieselstrasse, Germany) equipped with an M500 drive system and SV II coaxial cylinder sensor system. The temperature of the unit was controlled at 25°C by a circulating water bath. Casting solution (6 mL) was placed in the sensor and sufficient time allowed to reach thermal equilibrium. The shear stress was then determined at shear rates up to 445 s^{-1} depending on the composition of the casting solution under test. The zero-shear Newtonian viscosity of the casting solutions at 25°C was obtained from the resulting shear stress–shear strain curves.

Membrane Characterization

Operating conditions used for the solute sieving experiments have been reported previously (8). All separation experiments were performed in radial flow, crossflow test cells with a 508-μm gap thickness. The effective membrane area was 14.5×10^{-4} m^2. A recirculating feed flow rate of 3 L/min provided a crossflow velocity at the membrane surface of 0.8 m/s. Membranes were characterized at 344 kPa (50 psig) or 210 kPa (30 psig) depending on the pore radius of the membrane. Separation experiments were carried out using polyethylene glycols (PEG) of various molecular weights as the test solutes. PEG's with nominal molecular weights of 600, 1,500, 3,000, 6,000, 12,000, and 35,000 daltons were obtained from Fluka (Ronkonkoma, New York, USA). The combination of low feed solution PEG concentration (200 mg/L) and turbulent flow limits the influence of osmotic pressure and concentration polarization on the observed separations. Feed and permeate concentrations were determined using a Beckmann Total Organic Carbon analyzer (Fullerton, California, USA) that was automated in-house.

Model Fitting

Values for the average pore radius were obtained from a fit of the transport model to PEG separation data. The basis for an adequate fit was minimization of the sum of squares of residuals. The experimental results generated values of pore radius and $n/A\,\Delta x$ for discrete points on a grid of casting solution compositions. These points are represented by circles in the surface plots. A continuous response surface was generated from this data by a distance weighted least squares (DWLS) smoothing routine to allow interpolation between the grid points. Surface and contour plots were generated for both the pore radius and permeability parameter, $n/A\,\Delta x$, using the three-dimensional plotting package routines found in SYSTAT (Evanston, Illinois, USA).

RESULTS AND DISCUSSION

Table 1 presents solubility parameters for a number of solvents that were found to dissolve polyethersulfone. The total solubility parameter for polyethersulfone calculated from the center of a spherical solubility envelope was found to be 21.86 MPa$^{1/2}$. This is in reasonable agreement with values calculated by group contribution methods (11). On the basis of solubility parameter considerations, NMP is a good solvent for the PES system. Based on solubility considerations, PVP should form a miscible blend with PES as the solubility range of PVP overlaps that of PES. This

TABLE 1
Solubility Parameters of Victrex Polyethersulfone and Various Solvents (15)

Material	Dispersion (MPa$^{1/2}$)	Polar (MPa$^{1/2}$)	Hydrogen (MPa$^{1/2}$)	Total (MPa$^{1/2}$)
Benzonitrile	17.4	9.0	3.3	19.9
Bis(methoxyethyl)ether	14.3	6.7	6.7	17.1
Butyrolactone	19.0	16.6	7.4	26.3
Dichloromethane	18.2	6.3	6.1	20.3
Dimethylacetamide	16.8	11.5	10.2	22.7
Dimethylformamide	17.4	13.7	11.3	24.8
Dimethylsulfoxide	18.4	16.4	10.2	26.7
Acetophenone	16.1	11.9	8.2	21.6
Tetramethylurea	16.8	8.2	11.1	21.7
N-Methyl-pyrrolidinone	18.0	12.3	7.2	22.9
2(Methoxyethoxy)ethanol	16.2	7.8	12.7	22.0
Chloroform	17.8	3.1	5.7	19.0
Polyethersulfone (11), calculated	18.7	2.5	9.8	21.3
Polyethersulfone, experimental	17.6	10.4	7.8	21.9

result agrees with that suggested for Udel polysulfone by Cabasso et al. (12).

The viscosity of the membrane casting solution is an important parameter to be considered in membrane manufacture as well as having an influence on the ultimate membrane morphology. Viscous casting solutions are required in hollow fiber manufacture to maintain fiber integrity during the spinning process (12). It is impossible to produce hollow fibers if the solution viscosity is too low. On the other hand, in flat-sheet membrane manufacture, solution viscosity sets a practical operating limit for the spreading of the polymer solution on the backing. However, the solution viscosity must be sufficient to prevent excessive solution penetration into the porous backing materials used as supports for flat-sheet membranes. The casting solution viscosity also plays a role in the kinetics of formation of the coarse morphology of the ultimate membrane. Low viscosity casting solutions tend to produce membranes with fingerlike voids while viscous solutions produce membranes with dense sponge layers (13).

Figure 1(a) is a three-dimensional surface plot of the natural logarithm of the zero shear viscosity as a function of casting solution composition. Figure 1(b) is the corresponding contour plot. The viscosity of the PES casting solution can be effectively controlled by the addition of PVP, yielding solution viscosities as high as 90 mPa·s. This type of viscosity–composition plot provides an idea of the desirable operating region
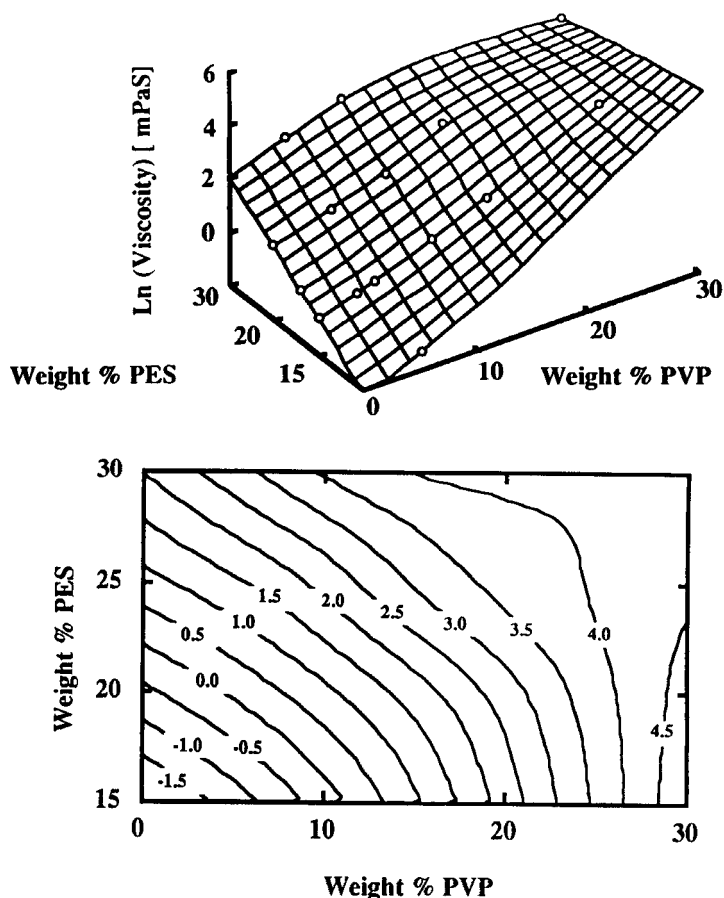
FIG. 1   Surface and contour plots of the natural logarithm of casting solution zero-shear Newtonian viscosity as a function of polyethersulfone and poly-(*N*-vinyl-pyrrolidone) content.

for membrane casting. In the present case, casting solutions for flat-sheet membranes should contain a minimum of 20 wt% PES and 10 wt% PVP.

Figure 2(a) is a plot showing the combined effect of PES and PVP concentration on the average pore radius. Figure 2(b) is the corresponding contour plot. An average pore radius of less than 2 nm was achieved for this casting solution system at high PES and PVP concentrations. The steepness of the contours indicates that increasing the polymer concentration results in a more rapid decrease in pore radius when the PVP content
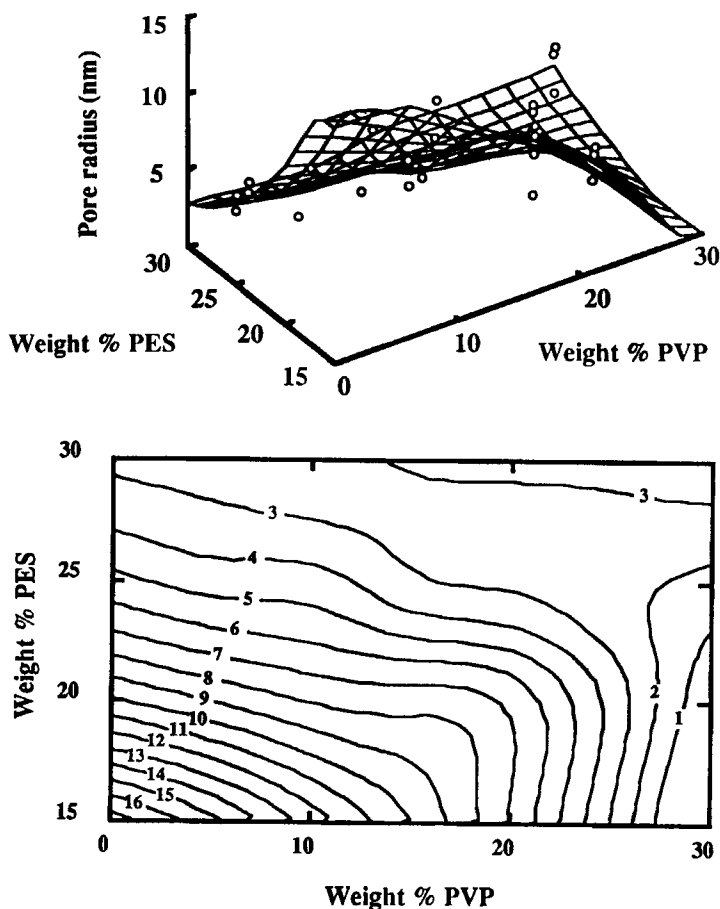
FIG. 2 Surface and contour plots of average membrane pore radius as a function of poly-ethersulfone and poly-(N-vinyl-pyrrolidone) content.

is less than 20 wt%. The pore radius decreases with an increase in either PVP or PES content for all other solution compositions.

These results are in qualitative agreement with the findings of Lafrenière et al. (4). The same PES:PVP:NMP casting system was considered, but unbacked membranes were produced by directly casting onto a glass plate. A transport model that incorporates both surface–solute interactions and a bimodal pore size distribution was used to analyze solute separation data. Although a detailed comparison of the two transport models is beyond the scope of this work, results from this study can be compared with

the authors' conclusion that an increase in either polymer concentration or PVP content can decrease the pore size. The three-dimensional plot confirms this effect. An increased polymer concentration of PVP or PES results in a denser membrane surface. This leads to a smaller pore size in the final membrane.

A three-dimensional surface plot illustrating the effect of casting solution composition on the ratio of the number of pores per unit area to the effective pore length appears as Fig. 3(a). The corresponding contour plot for this response surface is shown in Fig. 3(b). These plots show that large
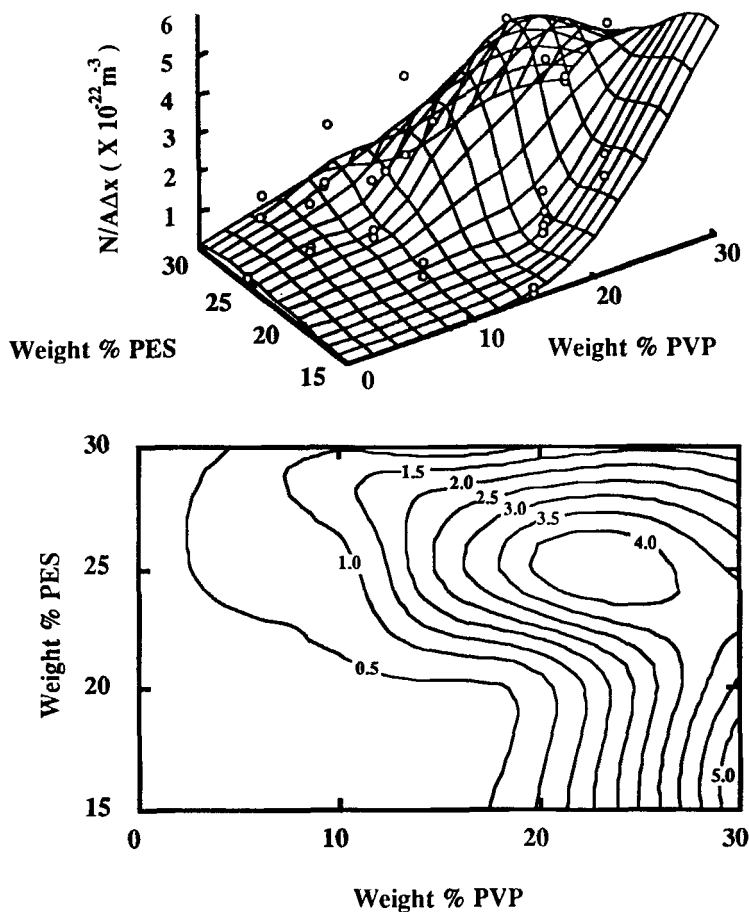
FIG. 3   Surface and contour plots of $n/A\,\Delta x$ as a function of polyethersulfone and poly-(N-vinyl-pyrrolidone) content.

numbers of pores or smaller pore lengths can only be obtained when PVP concentrations exceed 15%. The sensitivity of $n/A \Delta x$ to changes in PVP concentration is demonstrated by the steepness of the contours in this composition region. The value for the ratio is also large when both PVP and PES concentrations are high. The maximum value of $n/A \Delta x$ occurs where the concentration of both PES and PVP is 25%. This observation provides a physical explanation of the results reported by Lafrenière et al. (4). They concluded that the maximum product rate was obtained when the ratio of PVP to PES was close to 1. Figure 3 shows that maximum product rates are the result of high values for the ratio $n/A \Delta x$. The role of PVP is to increase the number of pores rather than to decrease the effective pore length. Scanning electron microscope images of Udel polysulfone have shown that high PVP concentrations produce a dense membrane without fingerlike voids (13, 14). This indicates that PVP is unlikely
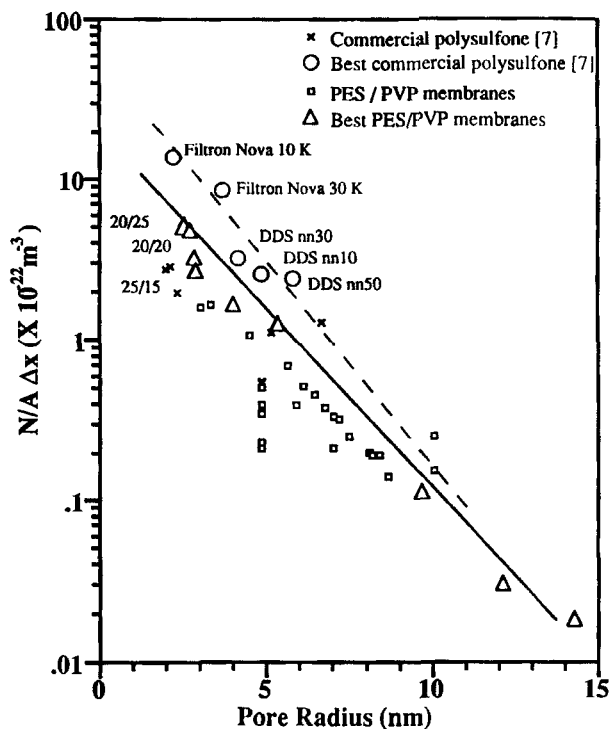

FIG. 4   Comparison of laboratory cast PES:PVP:NMP membranes with commercially available PES membranes.

to reduce the skin layer thickness. PVP serves to increase the polymer concentration in the membrane surface. Subsequent removal of PVP during the gelation step results in an increased number of pores in the membrane.

Figure 4 is a plot of the permeability parameter, $n/A\Delta x$, versus the average pore radius r_p. This figure allows direct comparisons of membrane performance. There is a compromise between the average pore radius and the permeability of a membrane. The performance limit for a membrane system is defined as the largest value of $n/A\Delta x$ for a membrane with a given pore radius. This limit for the present PES:PVP:NMP casting system is shown. Membranes from this casting system have the best performance when the PES concentration is greater than 20 wt% and the PVP concentration is also in the 20 wt% range. This system can be quantitatively compared to the performance of commercial PES membranes reported by Tweddle et al. (7). Filtron Nova series and DDS (NN-series) membranes have higher fluxes for a given average pore size than the present casting solution system. This indicates that these membrane manufacturers have developed proprietary formulations or casting techniques that produce membranes with performance superior to the laboratory-cast membranes used for this study.

CONCLUSIONS

Casting solution viscosities for the polyethersulfone:poly-(N-vinyl-pyrrolidone):N-methyl-2-pyrrolidinone system were reported as a function of changes in solution composition. Estimates of the average pore radius, r_p, and membrane permeability, $n/A\Delta x$, calculated using a simple transport model, varied significantly with changes in the polyethersulfone and poly-(N-vinyl-pyrrolidone) concentration of the casting solution. Membrane pore radius decreases with increasing concentrations of PES and PVP. Membranes with pore radii less than 2 nm were obtained for this system. Membrane permeability was significantly affected by the presence of PVP. For a given PES concentration, the addition of PVP increases the membrane permeability. The limiting performance for laboratory-cast polyethersulfone/PVP membranes was less than several commercial PES membranes which exhibited a higher permeability for a given average pore radius.

SYMBOLS

A area of the tested membrane coupon (m^2)
D_∞ diffusivity of solute in solution (m^2/s)

f	separation
n	number of pores
$\dot{P}e$	Peclet number
PWP	pure water permeation rate (kg/day)
Q	volumetric flow rate (m^3/h)
r_p	average pore radius (nm)

Greek

Δx	effective membrane pore length (m)
λ	ratio of solute radius to pore radius
ξ	ratio of restricted solute diffusivity within the pore to bulk solute diffusivity
η	solvent viscosity (Pa·s)
χ	global steric parameter
ΔP	pressure drop across the membrane pore (kPa)

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