The Effect of Polyethersulfone Concentration on Flat and Hollow Fiber Membrane Performance

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ABSTRACT

Flat and hollow fiber (HF) membranes are made in order to determine the effect of the polyethersulfone (PES) concentration in the precursor film-casting solution on resultant flat and hollow fiber membrane performance. The additive polyvinyl-pyrrolidone (PVP) is included in the film-casting solution to ensure that membranes can be made over wide variations in the PES polymer concentration. In general, membrane permeability decreases and solute separation ability increases as the PES concentration increases. However, for both flat and HF membranes, performance is strongly dependent on whether the PES concentration is above or below the critical value. Flux greatly decreases and solute-separation ability increases when the critical PES concentration is surpassed. Membrane performance is generally optimized when the PES concentration is at the critical value.

Key Words. Polyethersulfone; Macromolecules; Hollow fibers; Asymmetric membranes; Critical polymer concentration

INTRODUCTION

There are many commercially available polysulfone (PS) and PS-type membranes. PS membranes are known for their ability to withstand high

operating pressures and temperatures during use. A PS membrane can be made to separate very small molecules. A highly porous PS membrane can be made so that, for example, bacteria, organic detritus, or waste stream debris can be concentrated.

This paper is concerned with the effect of polymer concentration in a membrane casting solution on the performance of resultant flat and hollow fiber (HF) membrane products. In the Introduction, a review of the critical polymer concentration is made in order to estimate the critical concentration of the casting solutions used in this experiment. The method of making and testing flat and HF membranes is presented. In the Analysis, structure and performance of the membrane products are related to the composition and structure of the precursor casting solution, and to the membrane-making conditions.

Casting Solution Preparation

Materials

The materials for membrane preparation were chosen for their low cost and availability. The polymer, Victrex polyethersulfone (PES), was supplied by ICI. The medium molecular weight grade, 4800P, was used in this study. Since this is a commercial grade polymer, the molecular weight distribution is probably high. The solvent medium used for dissolution of the PES was dimethylacetamide (DMAc), obtained from BDH. A polymer additive, polyvinylpyrrolidone (PVP), with an average molecular weight of 10,000 g/gmol, was obtained from Aldrich. The membrane casting solution components were used as received, except the PES and PVP were dried in an oven for 3 hours at 130 and 65°C, respectively, to remove traces of water that may have adsorbed onto the polymer material.

Background

In general, a film of polymer solution is exposed to a solvent evaporation and gelation stage in order to produce a membrane product. The solvent and additive in a membrane casting solution are soluble in the gelation medium, but the polymer is not. In the gelation medium, the polymer solidifies and approaches a crystalline state. The final membrane product is composed primarily of polymer.

The performance of a membrane is dependent on the composition of the precursor casting solution. In this study, casting solutions of differing polymer concentrations were made. Table 1 lists the six casting compositions (H1 to H6) used in this study. The solution designated as H1 contains

TABLE 1
Casting Solution Composition and Concentration Data

	wt% PES	wt% PVP	wt% DMAc	g_{PVP} (g/cm³)	g_{PES} (g/cm³)
H1	12	20	68	0.276	0.136
H2	14	20	66	0.285	0.162
H3	16	20	64	0.294	0.190
H4	18	20	62	0.303	0.220
H5	20	20	60	0.313	0.251
H6	22	20	58	0.324	0.283

12 wt% PES. The PES concentration was increased by increments of 2 wt%, so that H6 contains 22 wt% PES.

Polyvinylpyrrolidone (PVP) is a typical additive for PES casting solutions. PVP is soluble in PES-DMAc solutions, even to a total solids content higher than 50 wt% (1). Also, PVP is soluble in water (2), the typical coagulant used in a PES membrane-making procedure. It is difficult to make flat or HF membranes from low viscosity polymer solutions. Therefore, a high PVP additive concentration (20 wt%) was used in each casting solution to increase the viscosity. This ensures that membranes can be made from a wide variety of PES polymer concentrations for a certain flat or HF membrane-making procedure. H1 and H6 are the limiting casting solution compositions for the experimental procedures used in this study. The high PVP content may influence membrane structure and performance.

The average PS concentration used for making flat membranes is 15 ± 2 wt%, and the typical PS concentration in HF solutions is 26 to 34 wt% (3). The PS/PVP ratio is usually from 1.5 to 2, so the range of solids content in HF casting solutions is from 40 to 52 wt% (4).

The PES concentration for solutions H1 to H6 is similar to that of typical flat membranes. However, the PS/PVP ratio is much smaller than other typical HF formulations. The total solids content of H1 to H6 is from 32 to 42 wt%. Since this is lower than the typical solids content in PS HF casting compositions, the solution viscosity is low and HF spinning is more difficult.

Theoretical

Generally, linear polymer molecules occupy their own domain in solution space when immersed in a suitable solvent. The viscosity of a polymer solution increases with increasing polymer concentration. Eventually, a

critical concentration is reached where the density of polymer macromolecules is so high that polymer–polymer contacts are inevitable. Above this critical concentration, a small addition of polymer to the solution causes a large viscosity increase.

The critical polymer concentration can be determined from the casting composition by the following equation (5):

$$g_x = 0.507d/\epsilon_x \qquad (1)$$

where g_x (g/cm^3) is the polymer concentration (g) at the critical point (x), d is the density of the crystalline polymer (g/cm^3), and ϵ_x is a swelling factor (ϵ) at the critical concentration, which accounts for the expansion of a macromolecule when in a suitable solvent. The swelling factor ϵ_x is determined from the following equation (5, 6):

$$\epsilon_x = 2.60 + (1.70 \times 10^{-4})Z \qquad (2)$$

where Z is the number of main chain atoms per polymer strand length. Equation (2) may be modified to account for the presence of additives that influence the overall solution structure (7).

Solution Structure Determination

Equations (1) and (2) are generally applicable to polymer in pure solvent. However, casting solutions contain the polymeric additive PVP. It is assumed there is a minimal energy of interaction between the PES and PVP macromolecules throughout the PES/PVP concentration ratios studied. This is generally supported by intrinsic viscosity data of Ref. 8 and solubility maps of Ref. 1. Also, the molecular weights of the PES and PVP used in this study are relatively small, which increases compatibility between the polymers (9). In dilute solutions, the volume pervaded by a macromolecule is generally unaffected by the presence of a compatible polymer (10). From the preceding comments, g_x for the PES and PVP macromolecules in film-casting solutions H1 to H6 can be estimated from Eq. (1).

Polyvinylpyrrolidone (PVP)

In the first stage of casting solution formulation, PVP is added to the DMAc solvent. The solutions are periodically shaken and kept warm in an oven at about 60°C for at least 2 days until there is complete mixing of the PVP in the DMAc. Note that for a constant wt% PVP, the PVP concentration (expressed in g/cm^3 of solvent) slightly increases as the PES concentration increases. Then g_{PVP} increases with a wt% PES increase. Table 1 lists the PVP concentration, expressed in g/cm^3, for solutions H1

to H6. For these calculations, the density of DMAc at room temperature is approximately 0.94 g/cm³.

The critical PVP concentration can be estimated from Eqs. (1) and (2). The magnitude of ϵ_x for PVP ($\epsilon_{x\,\text{PVP}}$) is approximated as 2.6 because the molecular weight of PVP is small and there are few main chain atoms per PVP strand length. The critical PVP concentration, $g_{x\,\text{PVP}}$, is approximately 0.24 g/cm³. To calculate $g_{x\,\text{PVP}}$, the bulk density of PVP polymer is 1.25 g/cm³.

Table 1 shows that g_{PVP}s for solutions H1 to H6 are above the critical PVP concentration. However, the PVP/DMAc solutions H1 to H6 are clear liquids and the solution viscosities are low. Then it is assumed the PVP macromolecules do not coalesce with each other to form a highly entangled solution, thereby resisting the dissolution of PES in the mixture. Intermolecular PVP–PVP contacts, if present, are assumed to be weak and transitory.

Polyethersulfone (PES)

The PES polymer is added after complete mixing of the PVP in DMAc. The solutions are kept warm in an oven at 65°C for at least 1 week, and periodically are shaken or mixed. The casting solutions are reduced to room temperature and filtered to remove impurities that are present in the commercial PES polymer. To filter, the solutions are pushed through three layers of fine nylon cloth by nitrogen at an operating pressure of 20 psig, although it was necessary for H6 to be filtered at 40 psig.

To determine the critical PES concentration, the specific gravity of PES polymer and DMAc solvent at 25°C are 1.37 and 0.94, respectively. The PES 4800P molecular weight is experimentally determined to be 50,300 g/gmol, and the number of main chain atoms (Z) is approximately 3035 (11). From Eqs. (1) and (2), the critical PES concentration is 0.2229 g/cm³.

Approximations are required to estimate g_{PES} for H1 to H6 compositions because the PES is added to a solution of DMAc that contains the additive polymer PVP. The PVP is above its critical concentration, so PVP occupies a large volume fraction of the solution space. Upon complete mixing, the PES is assumed to be completely dispersed among the PVP macromolecules.

High concentrations of PES can be added to a DMAc solution that contains a high concentration of PVP. This indicates that PVP–PVP intermolecular contacts are weak so that it is possible to thoroughly mix the PES throughout the solution. To facilitate mixing, the solutions are periodically agitated and kept in an oven at 65°C for 1 week. The elevated temper-

ature causes an increase in the total solution volume, thereby easing the dissolution of PES throughout the solution space. The elevated temperature may also weaken the PVP–PVP intermolecular contacts.

The concentration g is the ratio of the mass of polymer added to the volume of solution space that is available before the polymer has been added. In PVP–DMAc solutions, the total solution space is approximately equal to the sum of the PVP and DMAc volumes. For example, for H1, if 20 g (16 cm³) PVP are added to 60 g (63.8 cm³) DMAc, the resultant solution volume is approximately 79.8 cm³. The PES is added to the PVP–DMAc solutions to make solutions H1 to H6. Then g_{PES} is calculated by assuming the total solution space available for PES dissolution is the sum of the PVP and DMAc volumes. Table 1 contains values of g_{PES} for solutions H1 to H6, calculated by the above method.

From Table 1, $g_{x\ PES}$ is just slightly greater than H4 composition. However, $g_{x\ PES}$ is determined using a PES polymer molecular weight (M) that is determined from a gel permeation chromatographic technique. The actual PES molecular weight can vary significantly from this estimated value. However, if M is 30,000 g/gmol, $g_{x\ PES}$ is between that for the H4 and H5 compositions. If M is 70,000 g/gmol, then $g_{x\ PES}$ is slightly smaller than that for the H4 composition. Then the H4 composition is approximately at $g_{x\ PES}$, since the critical concentration is relatively independent of these variations in M.

Membrane Making

Flat Membrane Making

Flat membranes are made at room temperature (21–23°C) and approximately 55% relative humidity. A small amount of room temperature casting solution is poured onto one end of a clean rectangular glass plate. A thin film of polymer solution is made by slowly pulling the solution along the glass plate with a casting knife. The casting knife has a long, thin groove about its length so that a film of polymer solution remains as the knife is pulled along the plate. Similar films can be made by building up the sides of the glass plate with tape. A glass rod is then used to pull the solution along the plate, and a tape-width thickness of solution film remains.

The films are left to stand for 60 seconds and then are immersed into a tub of room temperature tap water. The DMAc and presumably most of the PVP are leached into the water, leaving a white membrane on the plate. The membrane gradually separates from the plate. The side of the membrane exposed to air for 1 minute is shiny; the other side is dull. This

probably indicates that skin formation occurs on the air-exposed side of the membrane. The higher the PES concentration in the casting solution, the shinier the skin.

The H1 membrane is thin and extremely fragile. As the PES concentration in the casting solution increases, the overall structural integrity of the membrane increases, so that H6 is a tough, durable film.

A milky-white, semi-opaque cloud emanates from the H1 surface upon immersion into the gelation bath water. The cloud volume and color in the gelation bath decrease as the PES concentration in the casting solution increases. Above $g_{x\ PES}$, clear, wavy streams of casting solution components flow out of the film surface and dissipate into the bath water.

The white cloud may contain PES as well as PVP and DMAc (8). PES–PVP contacts are predominant in solutions made below $g_{x\ PES}$ but above $g_{x\ PVP}$. PES–PES contacts to form an interconnected structure are hindered by the presence of large amounts of PVP, so some surface PES macromolecules can be leached into the gelation bath. As g_{PES} increases, the number of PES–PES contacts increases, which is observed by a decrease in the gelation bath cloud volume and color. It is then expected that below $g_{x\ PES}$, membrane solute-separation efficiency is low but increases with an increase in the PES casting concentration. Separation ability is predicted to be much greater if membranes are formed from solutions above $g_{x\ PES}$. By observation of the gelation procedure, flat membrane structure and performance are dependent on the PES casting concentration and whether it is above or below $g_{x\ PES}$.

A large amount of white precipitate is observed under H1 to H6 membranes in the gelation bath as they gradually lift from the glass plate. However, the thickness of the H1 to H6 membranes (0.25 mm) is almost equal to the thickness of the slit in the blade of the casting knife (0.28 mm). The volume occupied by the casting solution matrix does not significantly decrease with casting composition, solvent evaporation, or gelation effects. The membrane substructure must then be highly porous, and it serves primarily as a support for the denser surface layer.

The membrane is left to soak in a bath of room temperature tap water for at least 1 day. Circular sample coupons are cut from the membranes and mounted in a testing cell. Experiments are performed on H1 to H6 membranes in order to determine their respective flux and solute-separation ability.

Hollow Fiber (HF) Membrane Making

Hollow fibers are preferable to flat membranes because more membrane area can be packed into a certain module volume. Hollow fibers can be

formed with an excellent support structure so that they may be used at very high pressures. Hollow fibers are also more resistant to damage (12).

HF membranes are made by forcing polymer solution through a circular annulus. In the middle of the annulus is a hollow needle. A bore fluid, a coagulant for the PES, is forced by pressure through the needle. The annulus and bore needle housing is called a spinnerette. Some distance below the spinnerette is a coagulation bath where the HF settles and hardens. General details of spinnerette design and experimental set-up are given in Ref. 13.

The following are details of the HF-making procedure used in this study. The casting solution is poured into a stainless steel container. The container is connected to a vacuum pump for 15 to 30 minutes to draw out air bubbles that may be present in the casting solution. The container is then connected to an N_2 tank that provides pressure to force the polymer through the spinnerette. The membranes are made at room temperature (21–23°C) and about 55% relative humidity. The bore fluid and coagulation bath are room temperature tap water. The distance from the spinnerette to the coagulation bath is 80 cm. The bore fluid water is fed by gravity through the inner spinnerette needle at a rate of 16 ± 1 cm^3/min.

H1 to H6 hollow fibers can't be made at a constant N_2 pressure within the confines of this experimental procedure. The maximum N_2 pressure for the fabrication of HFs from the low viscosity H1 solution is 10 psig. The highly viscous H6 solution requires a minimum N_2 pressure of about 20 psig. Therefore H1 to H5 HFs are made at an N_2 pressure of 10 psig. It is very difficult to make an H5 fiber at 10 psig. The spinnerette opening continually plugs with the H5 casting solution, so H5 and H6 HFs are also made at 20 psig. An H6 HF is also made at 40 psig. The HFs are labeled according to their solution composition and casting solution extrusion pressure. For example, H5$_{20}$ is an HF made from the H5 solution at an N_2 pressure of 20 psig.

The lower viscosity solutions H1 to H3 have a very high rate (cm/s) of HF formation. The HF enters the coagulation bath and makes small coils. Coalescence occurs between adjacent strand sections if they touch each other. Therefore, before the fiber strand can coil, it is drawn from the first bath with a variable speed winding motor and dropped into a second room temperature tap water coagulation bath. The strands have solidified enough in the first bath so that coalescence between adjacent strands does not occur in the second bath. The HFs are left in a container of clean, room temperature tap water for at least 2 days.

As the PES concentration in the casting solution increases, there is an increase in the radius of the HF coil as it enters the first gelation bath. The H4$_{10}$ coil diameter is about 20 cm, and it settles gently to the bottom of the first bath. The slower rate of HF extrusion and larger coil diameter

allow enough time for sufficient coalescence to occur so that permanent contacts are not made between adjacent strands if they touch each other. A second gelation bath is not required to make H4 to H6 HF membranes, even at elevated N_2 extrusion pressures. The process of HF membrane formation is dependent on whether the casting solution is above or below the critical PES concentration.

The inner HF wall is quenched with bore water immediately upon exit from the spinnerette. It is not known whether PES is leached from the inner bore wall. The movement of water in the gelation bath is too rapid to observe whether PES emanates from the outer wall. However, after HF making, the bath water is very slightly cloudy. This may be due to the presence of PES particles in the gelation bath, but may also only indicate the presence of a large concentration of PVP and DMAc. The HF products are left in room temperature tap water for at least 2 days.

One end of a HF strand is plugged while it is immersed in the water bath. A stream of N_2 at 20 psig is pushed through the hollow fiber bore from the other end to test for leaks. Any section of HF is discarded if N_2 bubbles through the outside wall. The H1 fiber is weak, so most of it is rejected. As the PES concentration in the casting solution increases, the amount of rejected material decreases. Very few leaks are detected in HFs made from solutions above $g_{x\,PES}$, and these leaks are due to technical problems during the HF formation procedure.

The remaining hollow fibers are cut into approximately 60 cm lengths. They are immersed in a 50% glycerol–water solution for at least 2 days. The glycerol replaces water in the interstices of the hollow fiber material. Then the HFs can be dried without collapsing. It is possible that collapsed HFs can be restored to their original state by immersion in water for 2 to 7 days (1, 3).

A bundle (6 to 8) of HFs (each about 30 cm in length) are inserted into a 3 to 4 cm length piece of one-quarter inch i.d. plastic tubing. Five-minute epoxy is daubed around and between the HFs where they enter the plastic tubing. Care is taken to ensure that the end of the plastic tubing is completely blocked by HFs and epoxy. Therefore, any solution that enters the plastic tubing can only exit through the walls or bores of the hollow fibers. The other end of the testing bundle is potted into a length of plastic tubing by the same method. The bundles are mounted in a testing system, and experiments are performed on the H1 to H6 HFs to determine their respective flux and solute separation ability.

ANALYSIS

A linear polymeric phase inversion membrane with very high solute-rejection ability [i.e., reverse osmosis (RO) or good ultrafiltration (UF)

performance] usually has a skin layer. This is a concentration of solidified polymer macromolecules at the interface that is supported by a more porous substrate. The structure of the skin layer is what controls the performance of the membrane. The skin layer morphology is dependent on the casting conditions.

A typical skin layer is formed due to solvent evaporation steps in the film-forming procedure. Flat membranes H1 to H6 may have a typical skin layer since the evaporation period for membrane-making is 1 minute. However, the internal wall of the nascent hollow fibers are immediately quenched with bore fluid while the outer walls are exposed to air only briefly.

Skinned PS/PVP/DMAc flat and HF membranes can be made (1). Skin formation is inhibited if the polymer concentration is too low or if the additive concentration is too high (14). Casting solutions H1 to H6 contain a large quantity of PVP, which reduces the possibility of skin formation (3, 15). However, water is a very strong coagulant for PS/PVP/DMAc solutions. This can cause polymer macromolecules to concentrate and solidify at the interface to form a dense layer (15). If there is no skin or dense layer, membrane performance is dependent on the size, packing arrangement, and degree of coalescence of the solidified macromolecules in the membrane matrix (16).

Membrane Macrostructure

Sections of flat and HFs made from solutions H1 to H6 are observed under a stereomicroscope. The maximum magnification of the microscope is $160\times$, and therefore only gross structural observations can be made. The thickness of the skin layer of an asymmetric membrane is too thin to be observed by these microscopic methods.

Flat Membranes

Under a microscope, the surfaces of flat membranes H_1 to H_6 are shiny. No pores are detected on the surface. A preponderance (profusion) of pores (about 0.01 mm in diameter or less) are observed on the substructure that came into contact with the glass plate.

A cross section of the flat membranes reveals a dense surface layer supported by a highly porous substrate. The dense layer thickness increases as the PES concentration in the casting solution increases. The H6 dense layer is more than half the thickness of the membrane.

Hollow Fibers

HF Wall Structure. The outer and inner HF walls are shiny. Small, wavy striations are observed on the outer wall, possibly indicative of

pattern formation during coalescence. Sometimes straight lines are observed along the length of the inner HF wall. These may be due to burrs or scratches on the outer wall of the needle contained within the spinnerette.

A proliferation of pores are observed on the inner walls of the H4 to H6 fibers and outer walls of the H5 and H6 fibers. They are similar in magnitude to pores in the substrate of the flat H1 to H6 membranes. It is not known whether there is an opaque skin layer over the mouth of the pores. The solute separation ability of PS hollow fibers is too high for performance to be strongly dependent on pores of this magnitude. HF performance is either dependent on an opaque skin structure over the pore mouth or on the structure of the PES matrix surrounding the pores.

Overall HF Dimensions. The average outer diameter (o.d.), inner diameter (i.d.) and wall thickness (x) for each HF sample are measured under the microscope. Table 2 lists the dimensional data for HF membranes H1 to H6. Each value in Table 2 is the average of at least six separate measurements, taken at various distances along the HF strand length.

Table 2 shows that, for a certain spinnerette, HF dimensions are strongly affected by whether the PES concentration in the casting solution is above or below g_x PES. The i.d., o.d., and x of the H1 to H4 HFs are approximately equal. The i.d., o.d., and x quickly increase once g_x PES is surpassed. The overall dimensions of the H5 and H6 HFs remain approximately equal, independent of the casting solution extrusion pressure.

The overall hollow fiber dimensions are directly related to the spinnerette design. The inner diameter of the bore needle (which the internal coagulant water passes through) is measured to be 0.53 mm. In comparison, the average i.d. of HFs H1 to H4, made at or below g_x PES, are approximately 0.60 mm. The wall thickness of the steel needle is not

TABLE 2
Overall Hollow Fiber Dimensions

No.	o.d. (mm)	i.d. (mm)	x (mm)	i.d./(o.d.)^2 (mm)$^{-1}$
H1$_{10}$	1.16	0.58	0.29	0.43
H2$_{10}$	1.16	0.58	0.29	0.43
H3$_{10}$	1.15	0.60	0.28	0.45
H4$_{10}$	1.16	0.63	0.27	0.47
H5$_{10}$	1.50	0.75	0.38	0.33
H5$_{20}$	1.52	0.83	0.35	0.36
H6$_{20}$	1.53	0.83	0.35	0.35
H6$_{40}$	1.50	0.79	0.36	0.35

negligible. The outer diameter of the needle is measured to be 0.81 mm. From Table 2, the i.d.s of the H5 and H6 fibers are approximately 0.80 mm.

In the lower viscosity (H1 to H4) casting solutions, the polymer solution exiting the spinnerette annulus creeps across the space previously occupied by the wall of the bore needle to come in contact with the exiting bore water. Therefore, the i.d. of the HF approaches the inner diameter of the needle. The opposite occurs for the H5 and H6 fibers because the viscosity of casting solutions above g_x PES is much higher. The internal coagulant water exits the spinnerette and fills the wall space that was previously occupied by the steel of the needle. Above g_x PES, the i.d. of the HF is about equal to the o.d. of the bore needle.

The annulus of the spinnerette for the passage of casting solution is measured to be 2.09 mm. In comparison, the o.d.s of H1 to H4, and H5 to H6 HFs are approximately 1.16 and 1.51 mm, respectively. The H1 to H4 hollow fibers are significantly influenced by the low casting solution viscosities, extrusion pressure, gravity, and shear stress between the casting solution and the spinnerette, needle, and bore water walls. The o.d.s of the HFs may be smaller than the spinnerette annulus due to contraction of the HF material when gelated by a strong coagulant (15). The extrusion of solutions above g_x PES approaches plug flow. Note that i.d., o.d., and x are also strongly affected, for example, by the choice of additive used in the casting solution (1) and the flow rate of the internal coagulant (17).

The i.d., o.d., and x of a commercial HF are made to meet its specific application requirements. For example, an HF can be made with a thick wall for high pressure operation. A large i.d. may be required so that the fiber won't be clogged when ultrafiltering dirty waste streams (18). The o.d. of an RO fiber is extremely small (12, 17) to maximize the membrane surface area that can be packed into a membrane module volume. This is especially important for RO systems because the flow rate per area of membrane surface is small.

The i.d./o.d. ratio of some RO HFs is 0.5 or less (12, 17), probably to withstand the high pressures involved in desalination by membranes. The average i.d./o.d. for some experimental PS membranes is also 0.5 (1, 4), although the additive used in the casting solution can have a significant effect on i.d., o.d., and i.d./o.d. The i.d./o.d. ratios for the H1 to H6 HFs are also approximately 0.5.

The inner wall surface area of an HF membrane per volume of bundle is maximized when i.d. approaches o.d. and when the o.d. is very small. The inner wall surface area to total fiber volume is proportional to i.d./ (o.d.)^2. Table 2 lists i.d./(o.d.)^2 for the H1 to H6 HFs. Table 2 shows that

better packing efficiency occurs with the H1 to H4 HFs. This is mainly because the o.d. is smaller for the fibers made at or below g_x PES. From Table 2, optimal packing efficiency occurs with the H4$_{10}$ HF when the PES concentration is approximately g_x PES.

Internal HF Structure. Macroscopic observations of cross sections of the H1 to H6 fibers reveal many very thin striations that originate from the inner bore wall. These tunnels, or fingerlike intrusions, are due to the high strength of the inner bore coagulant and low casting solution viscosity (15). The coagulant water channels into the HF structure, and the surrounding PES in the casting solution matrix solidifies. Since adjacent water tunnels are simultaneously being formed, the water burrows radially from the HF core. The dark circles observed on the inner walls of the fibers are likely the entrances to each fingerlike intrusion.

Rapid coagulation of the inner wall casting material may cause the outer wall solution to increase in viscosity before immersion into the gelation bath water. This can inhibit fingerlike intrusion formation from the outer wall (15). In comparison to the literature, fewer intrusions are observed in the outer walls of the H1 to H6 fibers and the outer polymer matrix appears much denser.

The powerful bore coagulant may also cause macrovoids to form within the fiber, as is seen in the H1 and H2 HFs. These are relatively large empty pockets aligned equidistant from the HF core. Many small pores dot the surface of these macrovoids. The pockets may connect to form large fissures, as observed with the H3 HF. The spinning conditions are such that H3 often collapses toward the bore. Subsequent experiments revealed that many fibers made from low viscosity PES casting solutions will collapse if the inner bore water flow rate is too small.

The internal structure of the H4 fiber is quite dense. A faint circular boundary line is observed between the outer and inner walls of the fiber. This may be the point where intrusions emanating from the inner wall meet intrusions entering from the outer wall. Some intrusions from the inner wall of the H4 fiber travel past the boundary line and approach the outer wall.

The H5$_{10}$ HF is similar to a fiber within a fiber. This is caused by rapid solidification and contraction of the inner portion of the nascent fiber upon exit from the spinnerette (15). The casting solution that forms the outer HF portion can migrate along the solid inner portion before coalescing in the gelation bath. Many pores are detected on the outer wall of the inner H5$_{10}$ fiber, but are not observed on the inner wall of the outer fiber. The H5$_{20}$ HF is also usually a fiber within a fiber. In these fibers, many pores are detected on the outer wall of the inner fiber and inner wall of the outer fiber.

Many tiny macrovoids are dotted about the boundary line of the $H6_{20}$ fiber. No macrovoids are observed in the $H6_{40}$ fiber. The outer portion of the $H6_{40}$ fiber is very dense, although pores are detected on the outside wall of the fiber.

The hollow fiber cross-sections reveal that, under these spinning conditions, macrovoid formation is minimized when the PES concentration is at or above g_x $_{PES}$. Fingerlike intrusions are found in all fibers made from H1 to H6 casting solutions because the PVP content in the casting solutions is high, the casting solution viscosity is relatively low, and a powerful bore coagulant is used in the spinning procedure.

Flux Analysis

The H1 to H6 flat and HF membranes are tested with room temperature distilled water at operating pressures of 30 and 40 psig, respectively, in order to determine their rate of pure water permeation (PWP, $g/cm^2 \cdot h$). Table 3 lists some PWP data for the H1 to H6 flat and HF PES membranes. All data in Table 3 are corrected to 25°C.

Flat Membranes.   Table 3 shows the effect of the PES casting concentration and membrane compaction on flux through the membranes. Table 3 contains PWP data for H1 to H6 membranes after 30 minutes and 3 hours of use. Table 3 also contains PWP data at steady-state, i.e., when PWP does not vary with time. These values in Table 3 are the average of two membrane coupons tested.

Table 3 shows that flux through an uncompacted membrane is dependent on the PES casting concentration. The PWP decreases as the PES concentration increases, in comparison to the dense layer thickness variations observed under the microscope. However, steady-state PWP values for H1 to H6 membranes are generally similar. The membranes made below g_x $_{PES}$ compact considerably, and PWP at steady-state is 3 or more times smaller than the PWP after 30 minutes of compression. In comparison, water flux through the H6 membrane does not change much with use. The membranes made below g_x $_{PES}$ require a much longer time (about 16 hours) to approach a steady-state flux value. The membranes made above g_x $_{PES}$ require about 7 hours to reach steady-state.

Membrane coupons H1 to H6 are compressed for 3 hours at 30 psig. Solute separation tests are then conducted with the membranes. The PWP is measured before each solute separation test. The pump is turned off until the next test (usually the next day). For each membrane, the PWP remains essentially constant throughout the series of tests. Table 3 lists the average PWP values for membranes H1 to H6. The corresponding

TABLE 3
Flux Data for Flat and Hollow Fiber Membranes

PWP, g/cm²·h	Flat membranes[a]					
	H1	H2	H3	H4	H5	H6
a	91.9	70.9	67.7	57.3	40.3	34.0
b	64.0	44.2	49.0	39.8	28.9	28.5
c	31.5	17.4	22.4	34.7	24.9	26.1
d	41.5	32.5	42.4	39.5	29.2	25.3
	Hollow fibers[b]					
	$H1_{10}$	$H2_{10}$	$H3_{10}$	$H4_{10}$	$H5_{20}$	$H6_{20}$
e	13.1	11.9	11.0	8.4	3.6	3.4

[a] Operating pressure, 30 psig: (a) after 30 minutes; (b) after 3 hours; (c) steady-state value, upon complete compression; (d) average, during solute-separation tests.

[b] Operating pressure, 20 psig: (e) average, during solute separation tests.

solute separation data are in Fig. 1. The average PWP values for H1 to H6 membranes used for the solute separation tests are similar to the average value of the two coupons after compression for 3 or more hours.

The data in Table 3 show that steady-state flux is generally optimal with membranes made from H4 casting composition. Compaction of membranes H1 to H3 made from solutions below g_x PES is significant, so that PWP through these membranes is too small. On the other hand, the flux of uncompressed H5 and H6 membranes is already low, and compaction further reduces their PWP.

Hollow Fibers. Hollow fiber PWP data in Table 3 is the average from two bundles tested that provided the best selectivity of all bundles made from that particular casting solution composition. The corresponding solute separation data are in Table 4. Other bundles tested had higher PWP and lower selectivity. These differences can be significant, especially for H1 to H3 fibers made below g_x PES. The decrease in selectivity accompanied by an increase in flux may be caused by fingerlike intrusions from the inner and outer fiber walls that are connected to macrovoids or fissures in the boundary area. Some lengths of the $H5_{20}$ HF do not form a complete fiber within a fiber. These sections were tested, and the data are presented in Tables 3 and 4.

Table 3 shows that PWP for H1 to H4 hollow fibers gradually decreases as the PES concentration in the casting solution increases. A significant decrease in PWP occurs once g_x PES is surpassed. The increased wall
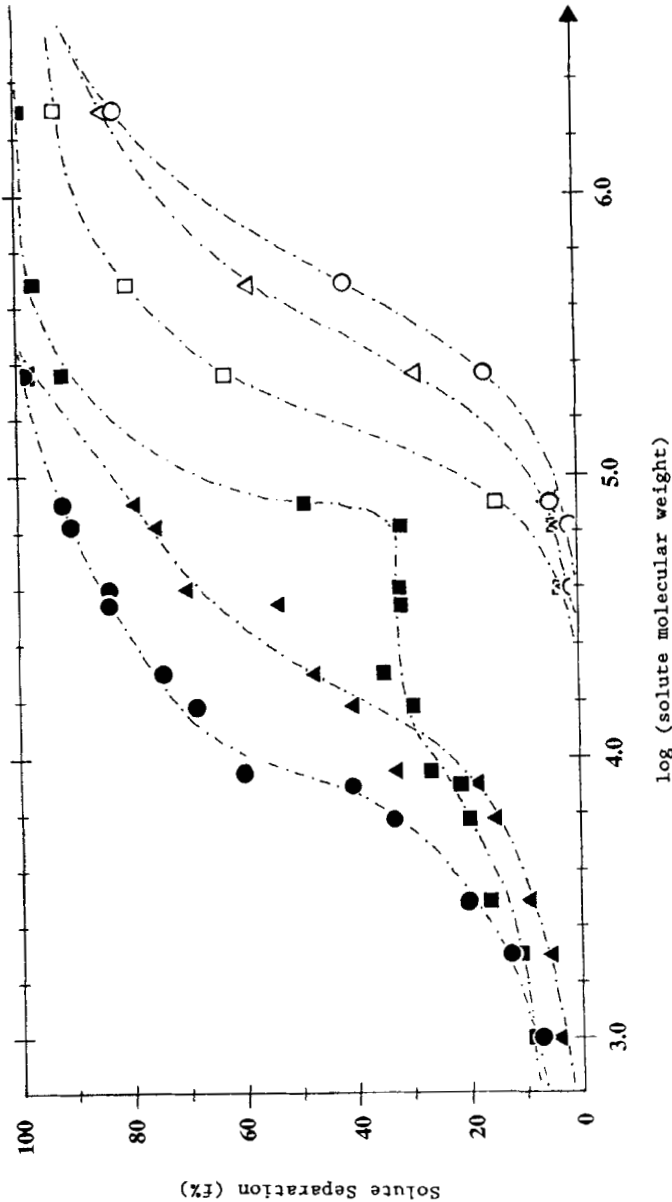
FIG. 1   Flat membrane separation ability versus solute molecular weight: (○) H1, (△) H2, (□) H3, (■) H4, (▲) H5, (●) H6.

TABLE 4
Hollow Fiber Separation Data

PEG solute M (g/gmol)	Solute separation ($f\%$)					
	$H1_{10}$	$H2_{10}$	$H3_{10}$	$H4_{10}$	$H5_{20}$	$H6_{20}$
1,000	20.0	13.8	45.9	16.5	13.0	13.1
2,000	43.8	22.6	46.6	48.8	46.0	48.9
3,110	64.4	57.8	74.9	77.5	71.3	81.1
4,000	74.4	56.9	—	86.3	91.6	88.5
6,000	78.1	80.9	73.2	93.5	95.5	95.2
8,000	77.1	92.4	79.0	96.0	94.5	96.5
10,000	79.4	—	84.7	98.1	97.4	98.8
12,000	84.0	—	82.5	—	—	—
15,000	87.0	95.7	83.3	—	—	—
20,000	92.2	96.3	84.7	—	—	—
35,000	93.2	98.4	96.4	—	—	—
Polyfon O	100	100	100	100	100	100

thicknesses of the H5 and H6 fibers do not account for the significant decrease in flux. As with flat membranes, performance-determining PES HF structure is dependent on whether the precursor casting composition is above or below g_x PES.

The pure water fluxes through H1 to H6 hollow fibers do not decrease with time. Unlike flat membranes, HFs are not supported on one side by a rigid substrate, so they do not compact during use. A small PWP increase with time was observed with some fibers. Some PVP or glycerol may have remained in the fiber matrix initially, but is eventually leached into the feed or permeant water during use.

Solute Separation Tests

The solute-separation ability of the membranes are determined with solutions composed of room temperature distilled water containing 0.2 g/L of various molecular weights (M) of polyethylene glycol (PEG) solute. For example, a PEG 6000 solution indicates an average PEG molecular weight of 6000 g/gmol. Dextran solutions are used if separation tests are required with solutes of molecular weights greater than 40,000 g/gmol. Separation is determined with a carbon analyzer, where the carbon content of the solute in the feed solution is compared to the carbon content of the permeant:

$$f\% = \left(\frac{\text{feed concentration} - \text{permeant concentration}}{\text{feed concentration}}\right) \times 100 \quad (3)$$

Flat Membranes.   Figure 1 is a plot of the solute-separation ability of flat H1 to H6 membranes versus the log of the solute molecular weight. For each membrane, $f\%$ slowly increases with an increase in M until a point is reached where a small increase in the solute M causes a large increase in $f\%$. When solute-separation ability is high, $f\%$ again gradually increases with M as complete separation is approached. Each curve is roughly S-shaped, indicating more than one average pore size distribution on the membrane surface (19).

Figure 1 shows that the PES content in the casting solution strongly influences membrane performance. For example, for H1 membrane, $f\%$ is approximately 5 and 82% for Dextrans of 78,500 and 2,000,000 g/gmol, respectively. For H6 membrane, $f\%$ is approximately 7 and 84% for PEG solutes of 1000 and 35,000 g/gmol, respectively. The overall solute-separation ability of the membrane increases as the PES concentration in the casting solution increases.

An increase in membrane selectivity with a PES casting concentration increase is predicted for H1 to H3 membranes by observing the clouds emanating from the film surface during the film-forming procedure. Films made from solutions below g_x PES yield microfiltration (MF) or low perfor- mance ultrafiltration (UF) membranes. Supermolecular structures likely detach from the film surface upon immersion into the gelation bath water, yielding macrovoids in the membrane skin layer that travel into the sub- strate (20). Since selectivity increases from H1 to H3, the size and number of macrovoids is dependent on the PES casting concentration.

Cloud formation is not observed in the gelation stage when H4 to H6 membranes are made. Note from Fig. 1 that there is a dramatic increase in membrane selectivity when the casting composition is at or above g_x PES. The solute separation ability of the flat membranes is dependent primarily on whether the casting solution is above or below the critical PES concentration.

The rate of solute-containing permeant (PR, g/cm²·h) may be smaller than PWP, depending on properties such as solute molecular weight. For H1 to H3 membranes, PR becomes considerably smaller than PWP when the solute M is more than 50,000 g/gmol. The H4 to H6 membranes are influenced by solutes greater than 8000 g/gmol. This trend is expected because the smaller pores resulting from solutions made above g_x PES are more affected by lower M solutes. When very large solutes are used in the solution, the ratio PR/PWP is lower for H1 to H3 membranes than for the membranes made above g_x PES.

Some solute separation tests are performed on the flat membranes that have been compressed until an equilibrium PWP is achieved. In general, the compressed membranes provide somewhat better selectivity, but at the expense of flux. The increase in $f\%$ ability, compared to membranes

compressed for only 3 hours, varies widely with each membrane coupon tested. The selectivity of H1 to H6 flat membranes is somewhat dependent on their substructure.

Flat membrane performance was also tested with 0.2 g/L solutions of Polyfon O (a commercially-available sulfonated lignin found in waste streams in the pulp and paper industry) and a red dye (FD&C #40, M approximately 470 g/gmol). For both solutes and all membranes, separation is from 90 to 96%. For each solute type, selectivity very slightly increases as the PES casting concentration increases. Flux through membranes made above g_x PES is slightly affected by the presence of these solutes in the solution.

Hollow Fibers. Table 4 contains PEG solute-separation data for some H1 to H6 fibers. Each value in Table 4 is the average of two measurements from different bundles. Separation data in Table 4 correspond to the bundles used to obtain the PWP values in Table 3. Flux through the hollow fibers is not significantly affected by the presence of low concentrations of PEG solutes in the feed solution.

From Table 4, the selectivity of the H1 to H3 fibers is greater than that for the H6 flat membrane (Fig. 1). It is interesting to note that even a 1-minute evaporation period does not enhance skin formation enough to produce flat membranes with greater selectivity than their hollow fiber counterparts. Due to its high boiling point, little DMAc would evaporate during a 1-minute, room temperature solvent evaporation period. In comparison, some aromatic polyamide desalination membranes are made by evaporating DMAc from a film of casting solution in an oven at 95°C for 15 minutes (7). The high PVP content in H1 to H6 casting solutions also inhibits final PES skin structure integrity.

Hollow fibers may have higher selectivity than their flat membrane counterparts due to the structure of the PES matrix that constitutes the fiber. With the fibers used for the data of Tables 3 and 4, fingerlike intrusions are not linked from the inner to outer HF wall. However, macrovoids in the skin layer of H1 to H6 flat membranes may be directly connected to the porous substrate, dependent, for example, on the additive–solvent combination in the casting solution (20).

From Table 4, the selectivity of the H4 to H6 HFs are similar. The solute-separation abilities of these fibers, made from casting solutions above g_x PES, are significantly higher than those from fibers H1 to H3. HF selectivity is dependent primarily on whether the casting solution is above or below the critical PES concentration.

The $H5_{10}$ and $H5_{20}$ fibers within fibers have a selectivity similar to that of the H1 HF. The performance of H1 to H3 fibers can also vary considerably with each strand section tested, and may approach the performance characteristics of the H6 flat membrane. However, there is high

selectivity and reproducibility with the H4 and H6 fibers. These observations show that macrovoids, fissures, collapsed fibers, or fibers within fibers may lead to poor HF performance and fiber reproducibility. Large pores are formed by connections from the inner to outer HF wall via these imperfections. But selectivity and reproducibility of a fiber can be high, independent of the presence of fingerlike intrusions.

The H1 to H6 fibers are tested with a 0.2 g/L solution of sulfonated lignin Polyfon O. Complete separation occurred with all the fibers, within the detection limits of the experimental procedure.

The $H4_{10}$ fiber provides the best performance of all membranes made and tested. Its flux is optimal while the solute-separation ability remains high. There is good fiber reproducibility. There are no macrovoids or fibers within fibers. The walls are thin in order to maximize internal HF surface area. Its performance is similar to that of a high flux hemofiltration membrane. Successful cell-immobilization experiments have been completed with $H4_{10}$ HF modules at the Department of Chemical Engineering, University of Ottawa.

CONCLUSIONS

Flat and hollow fiber membranes are made from PES/DMAc casting compositions that contain a high concentration of PVP. Various experiments are performed on the membranes in order to determine their performance ability. In general, flux decreases and selectivity increases as the PES concentration in the casting solution increases. A flat membrane has a significantly higher flux and lower selectivity than its hollow fiber counterpart.

The structure and performance of a flat or hollow fiber membrane is strongly dependent on whether the precursor casting composition is above or below g_x PES, the critical PES concentration. Membrane selectivity dramatically increases if membranes are made at or above g_x PES. The critical PES concentration can be estimated by calculation or by observing the flat or hollow fiber membrane-making procedure.

Optimal membrane performance occurs when the casting concentration is approximately at g_x PES. These membranes have high selectivity and relatively high flux. The thin-walled $H4_{10}$ fiber provides the best ultrafiltration performance of the flat and hollow fiber membranes tested.

ACKNOWLEDGMENTS

REFERENCES

1. I. Cabasso, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.*, *20*, 2377 (1976).
2. S. Munari, A. Bottino, G. Capanneli, P. Moretti, and P. PetitBon, *Desalination*, *70*, 265 (1988).
3. I. Cabasso, K. Q. Robert, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.*, *21*, 1883 (1977).
4. I. Cabasso and A. P. Tamvakis, *Ibid.*, *23*, 1509 (1979).
5. A. Rudin and H. K. Johnston, *J. Paint Technol.*, *43*(559), 39 (1971).
6. S. H. Maron and T. T. Chiu, *J. Polym. Sci.*, *Part A*, *1*, 2651 (1963).
7. T. D. Nguyen, K. Chan, T. Matsuura, and S. Sourirajan, *Ind. Eng. Chem.*, *Prod. Res. Dev.*, *24*, 655 (1985).
8. L. Y. Lafreniere, F. D. F. Talbot, T. Matsuura, and S. Sourirajan, *Ind. Eng. Chem. Res.*, *26*, 2385 (1987).
9. R. L. Scott, *J. Chem. Phys.*, *17*(3), 279 (1949).
10. P. J. Flory, *Ibid.*, *17*(3), 303 (1949).
11. T. Miyano, T. Matsuura, and S. Sourirajan, *Chem. Eng. Commun.*, *15*, 11 (1990).
12. E. I. du Pont de Nemours & Co., "Why Hollow-Fiber Reverse Osmosis," *Chem. Eng.*, p. 57 (November 29, 1971).
13. T. Liu, D. Zhang, S. Xu, and S. Sourirajan, *Sep. Sci. Technol.*, *27*(2), 161 (1992).
14. R. E. Kesting, *J. Appl. Polym. Sci.*, *17*(6), 1771 (1973).
15. I. Cabasso, E. Klein, and J. K. Smith, *Ibid.*, *21*, 165 (1977).
16. L. Broens, D. Bargeman, and C. A. Smolders, *Proc. 6th Int. Symp.*, *Fresh Water from the Sea*, *3*, 165 (1978).
17. R. McKinney, *Desalination*, *62*, 37 (1987).
18. B. R. Breslau, E. A. Agranat, A. J. Testa, S. Messinger, and R. A. Cross, *Chem. Eng. Prog.*, *71*(12), 74 (1975).
19. S. Sourirajan, *Lectures on Reverse Osmosis*, *1983*, Division of Chemistry, National Research Council, Ottawa, K1A 0R6, Canada, Chap. 4.
20. A. K. Fritzsche, B. L. Armbruster, P. B. Fraundorf, and C. J. Pellegrin, *J. Appl. Polym. Sci.*, *39*, 1915 (1990).