Polysulfone Hollow Fibers. I.   Spinning and Properties

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Synopsis

The development of porous polysulfone hollow fibers and the spinning process used are discussed. An analysis is given of the spinning parameters which determine fiber mechanical properties and permeability. Hollow fibers were prepared which display high modulus and high tensile strength. These fibers can withstand hydraulic pressures of more than 1000 psi. They can thus serve as supports for dense, ultrathin membrane coatings, useful in high-pressure reverse osmosis and ultrafiltration processes.

INTRODUCTION

The development of various types of hollow fibers and the comparative advantages of flat sheet and hollow fiber configurations have been reported.[1]

However, most of the information that directly relates to hollow fiber production has been reported only in the patent literature. In the present paper, we wish to report the results of our studies on the spinning and development of polysulfone hollow fibers, and to elaborate on the variable parameters that are involved in a hollow fiber spinning process.

The development of polysulfone hollow fibers (PSHF) for reverse osmosis and ultrafiltration was initiated after it was shown that flat sheet porous polysulfone provides an excellent support for very thin, highly selective water desalination membranes. Reported desalinations of simulated sea water with coated polysulfone porous support (in a flat sheet form) under pressures up to 1500 psi have resulted in high fluxes of 20–30 gfd (gal/ft²-day) and salt rejections of 95–99.8%.[2] Previous work from this laboratory had demonstrated the feasibility of spinning polysulfone hollow fiber[3] that could withstand such pressures.

The preparation of porous hollow fibers cannot be approached by the same method that led to successful casting of the flat sheet porous support. Hollow fibers must be mechanically self-supporting and must not collapse under operating pressures. Some a priori calculations are necessary concerning the mechanical response of polymers to the process of spinning to form hollow fibers.

Mechanical Response Considerations

The theoretical failure stress of plastic tubules has been found to correlate with their dimensions and with Young's modulus of the material according[4]

to the equation

$$Pe = \frac{2E}{(1 - v^2)} \frac{t^3}{\overline{OD}^3} \tag{1}$$

where Pe is the failure pressure (or the collapse pressure), E is Young's modulus, v is the Poisson ratio, t is the wall thickness, and $\overline{OD}$ is the outside diameter of the tube, with all the units consistent. For a polymer like polysulfone with a Poisson ratio of approximately 0.3, the ratio of failure pressure to Young's modulus increases as the cube of the ratio of wall thickness to outside diameter.

The modulus of unplasticized, extruded polysulfone used in this study varies from approximately 360,000 psi to 400,000 psi. However, the modulus of the porous material must be significantly less than the modulus of dense polysulfone, since a high void fraction reduces the load-bearing elements available in the fiber wall. This reduction of the modulus, and of the failure tensile strength, is a function, among other things, of the size and frequency of the pores in the fiber wall. If the reduction in modulus is a factor of 2 and one takes, for example, as an initial goal a ratio of wall thickness to outside diameter of 1:4, then the failure pressure would be

$$Pe = \frac{2 \times 180,000}{0.91} (\tfrac{1}{4})^3 = 6181 \text{ psi}.$$

The failure pressure is thus a function of the interaction of the porosity of fiber wall (through its influence on the tensile modulus) and the dimensions of the fibers. Since the fiber dimensions that result from a given extrusion procedure also affect the fiber porosity, the three factors—dimension, porosity, and failure pressure—are closely linked.

EXPERIMENTAL

Spinning

Fiber spinning for this program utilized a tube-in-tube jet; the dry–wet spinning technique was employed. This process utilizes a very short air quench exposure with ultimate gelation of the polymer thread in a subsequent nonsolvent bath. There are many parameters that influence the properties of the spun fibers. In this study, polysulfone hollow fibers with diverse properties were spun by varying spinning conditions. The principle steps of the process are shown in Figure 1 and are described herein:

1. A viscous solution (5,000–500,000 cP 50°C) of polysulfone in solvents such as DMA (dimethylacetamide) or DMF (N,N-dimethylformamide) was prepared. Often, a compatible second polymer was added to increase the solution's viscosity and to assist in other fiber-forming properties. Such a second polymer must be miscible with polysulfone solution (to give a coherent homogeneous blend) and it must be soluble in the quench media. The preferred solution found consists of three components: (1) polysulfone (Union Carbide, 1700 or 3500), (2) poly(vinylpyrrolidone) (PVP), and (3) dimethylacetamide (DMA).
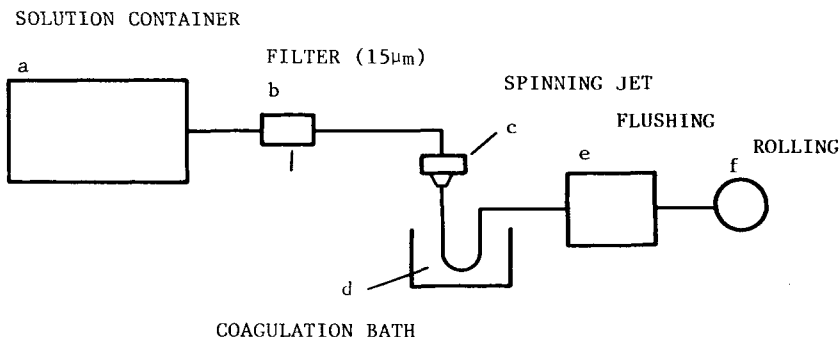
SOLUTION CONTAINER

Fig. 1. Schematic of hollow fiber spinning.

2. The spinning solution is prefiltered and then filtered again with a 15-μm line filter while being pumped to the spinning jet.

3. The solution extruded through the spinning jet is drawn into a coagulation bath; the center bore of the falling solution is maintained open by the use of a coagulant fluid under pressure. The cooling and the presence of coagulant in the bore cause the solution's viscosity to increase as it is extruded.

4. The coagulation of the nascent fiber proceeds from both the outside and inside surfaces. Various coagulation agents were used in the inside core, e.g., air, water, isopropranol, a combination of DMA/H$_2$O, and other agents. The outside quenching was by air, followed by a water quench bath. In some cases the quench bath contained 2 wt-% DMA, or 0.1–1 wt-% surfactant such as sodium dodecyl sulfate.

5. The nascent fiber solidifies in the coagulation bath and can be further handled. In most cases, the fiber is directly transferred from the bottom of the coagulation bath on to a self-advancing godet. The godets advance the fiber by lifting and shifting rather than by rolling the yarn; thus, the godet speeds determine the withdrawal rate of the yarn from the jet. The fibers are washed with hot water (60°C) to remove additives and solvents and are collected on a pirn.

Mechanical Measurements

The failure stress, the failure strain, and the elastic modulus were obtained by measurement with an Instron Universal Tester, using a 5-cm gauge length and a strain rate of 1 cm/min. The experimental fibers were clamped with rubber-faced hydraulic jaws. Five replicates were strained to failure. An Instron integrator was used with later specimens to provide the work of rupture. In the tables that follow, the measured force values are reduced to tensile values by correction for the cross-sectional area of the specimens, i.e.,

$$\text{tensile strength} = \frac{\text{breaking force} \times 4}{\pi(\overline{OD}^2 - \overline{ID}^2)} \qquad (2)$$

where $\overline{OD}$ and $\overline{ID}$ are the outside and inside diameters, respectively, as measured in a calibrated microscope at 150X magnification. Scanning electron microscope pictures were used for confirmation on some specimens and for examination of the microstructure.

"Maximum Pore Size" Determination

Maximum pore size was determined by the "bubble breakthrough measurement" according to ASTM E-128-61 (reapproved 1969) procedure. The technique is described in detail in various publications.[5]

Water Flux Measurements

Ultrafiltration rates were determined by steady-state measurement of the quantity of water permeating a fiber bundle at a pressure of 4 psi. The fiber bundles contain approximately 100 fibers which are potted either into a ½-in.-diameter polypropylene tubing or a ⅜-in. steel tubing. Swagelock fittings were used to connect the experimental bundle from each end to an air-pressurized 10-ml buret filled with water. In this system, water flows into the internal core of the fibers and permeates from the internal to the external side of the wall.

The hydraulic permeability L_p of the polysulfone hollow fiber was calculated from the flux equation:

$$J = AL_p\Delta P \tag{3}$$

where J = permeation rate (cm^3/cm^2-sec), A = area (cm^2) of the measured polysulfone hollow fiber, and ΔP = differential pressure applied, i.e., ($P_{external} - P_{internal}$) (atm).

Potting and Test Procedures for High-Pressure Testing of Polysulfone Hollow Fibers

Techniques were developed for high-pressure testing of fiber bundles containing 50 to 100 fibers of approximately 25-cm lengths. This size fiber bundle was selected because it contains enough fibers and surface area to give a representative average of a particular fiber spinning. The procedures used can be readily scaled up to evaluate much larger bundles as the test program dictates.

It was necessary to evaluate several potting resins to obtain one that would satisfy the requirements for high-pressure testing. Some of the criteria considered in selecting resins for evaluation were: reasonable cure times, adhesion to the stainless steel tubing in which the fiber is secured, low viscosity (which aids in successfully potting all fibers in the bundle), lack of fiber wall penetration to avoid blockage, and the absence of creep at 1000 psi. Epoxy resins were the most promising resins of those tested. All pottings with silastics and polyurethanes failed, usually at the bond between the resin and the stainless steel sleeve, when subjected to high pressure. Several epoxy resins were found satisfactory. The one which was used in this study was Stycast 1266, a product of Emerson and Cuming. Testing cells are shown in Figure 2.

The potted bundle is locked in place inside the cell. The feed solution enters by a T-connection at one end and leaves the cell by a similar connection at the other end. Pressure is applied to the outside of the fibers. The product which permeates the fiber wall migrates to both ends of the fiber bundle, where it is collected for analysis. These cells are mounted in a typical reverse osmosis rig.
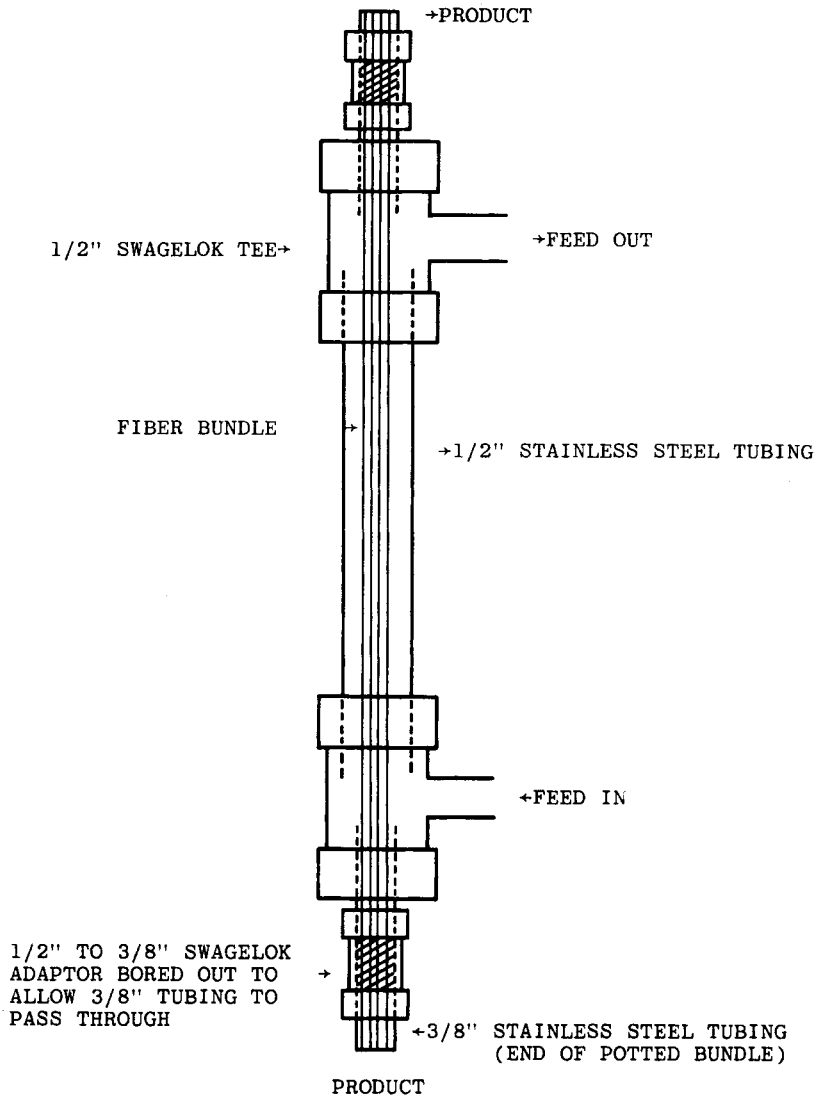
Fig. 2. High-pressure test cell for 100 cm^2 fiber area.

RESULTS AND DISCUSSION

The failure pressures calculated from the mechanical data and eq. (1) indicate that the fibers should be useful for reverse osmosis at elevated pressures. However, the requirements of a suitable support fiber for ultrathin coatings or ultrafiltration include not only the mechanical factors, but also morphologic characteristics. Thus, a satisfactory spinning process must provide fibers having the requisite permeability, surface pore size, and stability under long-term compression. The spinning process requirements that control these factors are complex. Many parameters are involved, and these parameters interact during the extrusion/coagulation steps. The principal variables are the following: (1) solution composition, (2) solution viscosities, (3) spinning temperature, (4) solution pumping rates, (5) coagulation agents (inside and outside), (6) coagulation temperature, (7) "nascent fiber drawing rate."
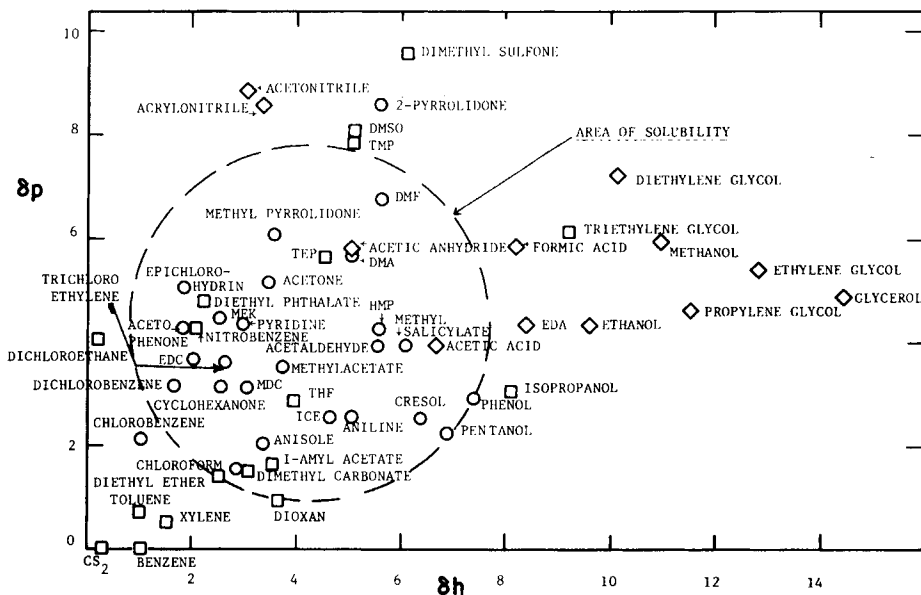
Fig. 3. Polysulfone solubility map: (O) soluble; (□) swell; (◇) insoluble.

Polysulfone Spinning Solution

Polysulfone solubility is represented in the two-dimensional Hansen's[6] solubility parameter diagram (Fig. 3). The plane is defined by δ_p and δ_h coordinates, which represent the polar and hydrogen interaction fraction of the Hildebrand solubility parameter δ. (The correlation is given by the equation $\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2$, where δ_d is the dispersion forces component of δ.) Each organic compound can be identified by its location in the plane according to its solubility parameter values. The confined area is that of polysulfone, and is defined by the location of compounds which are solvents to this polymer.

The selection of proper solvents for spinning polysulfone hollow fibers involves the following considerations: (1) the solvent must be miscible with the coagulating agent; (2) the solvent must provide good mechanical properties to the formed yarn upon quenching. Previous data have shown that a solution of polysulfone in DMF, when cast on a glass plate and quenched in water, provides porous film which can successfully support ultrathin membrane under elevated hydraulic pressures. However, the formulation for casting the flat sheet membrane is not adequate for the spinning process. The flat sheet polysulfone porous membrane is usually cast from solution that contains 15 wt-% of the polymer in DMF and is subsequently quenched by water. This procedure is satisfactory for flat sheet membranes which, subsequently, under operation conditions are mechanically supported by sintered rigid support. However, hollow fibers must be mechanically self-supporting. An increase of the polysulfone concentration in the solution was found to be essential for the spinning process to provide the correct texture to the ultimate fiber. A related problem is the viscosity of the spinning solution. A polymeric solution can be cast on a support surface to form a film from very dilute solutions as long as some minimum surface tension is main-

TABLE I
Spinning of PSHF with Various Additives

Additive (10 wt-%)	Viscosity cP	Hydraulic permeability $L_p \times 10^5$, cm/sec-atm	Inside diameter μm	Wall thickness, μm	Pore size range, μm
PVP	12640	31	243	53	0.19–0.25
Me Cellosolve	2223	154	101	106	0.44–0.28
PEG	4660	leaked	216	86	large

tained to keep the mechanical integrity of the layer. In the spinning process, the nascent fiber is supported only by the solution viscosity. A minimum of several hundred cP viscosity is required to stabilize the formation of polysulfone hollow fiber. Spinning solutions with viscosities up to 500,000 cP (50°C) were utilized in this study. Such high viscosities are often required in order to eliminate the formation of intrusive macrovoids in the fiber walls.

To achieve the proper viscous solution, one can choose among three alternatives: (1) increasing the polymer concentration and/or molecular weight; (2) employing solvents that are near the solubility area boundary (poor solvents); (3) incorporate a third component into the spinning mixture, to induce elevated viscosities. The solubility diagram (Fig. 3) indicates that DMF, DMA, and acetone are suitable solvents for the spinning process if water quenching is applied. Dimethylacetamide (DMA) was the preferred solvent because of its high boiling point and because it is a better solvent than DMF (according to the diagram). In such a spinning procedure, it is recommended that good solvents be used which have the power to open and solvate the polymeric chains.

Various additives (third component) have also been investigated. These include Methyl Cellosolve, glycols, fatty acids, poly(vinylpyrrolidone) (PVP) and polyethylene glycol (PEG-600Mw). Three of these gave suitable solutions from which polysulfone hollow fibers could be spun: Methyl Cellosolve, PEG, and PVP. Table I shows comparative data for these three systems.

The fibers spun with Methyl Cellosolve had much higher hydraulic permeabilities and much larger pore size than similar fibers spun with PVP. The viscosity of the Methyl Cellosolve solution was about one sixth that of the PVP solution.

The fibers spun similarly with PEG were found to have large, intrusive, crescent-shaped macrovoids in the fiber wall which collapsed under elevated hydraulic pressures. The viscosity of this mix was about one third that of a similar PVP mix.

Poly(vinylpyrrolidone) (PVP) was found to be the preferred additive. This is in agreement with previous work from this laboratory.[3] The solubility map of PVP is shown in Figure 4. Overlap of the solubility areas of the two polymers, PVP and polysulfone, is shown in Figure 5. This overlap explains[7] the high compatibility of the two polymers. No "cloud point"[8] (phase separation) was observed in solutions of these two polymers in DMA or DMF, even when the solution contains more than 50 wt-% solids (polymers).

The term solid content is often used in the present paper instead of polymer concentration. This is to emphasize the quantity of those ingredients in
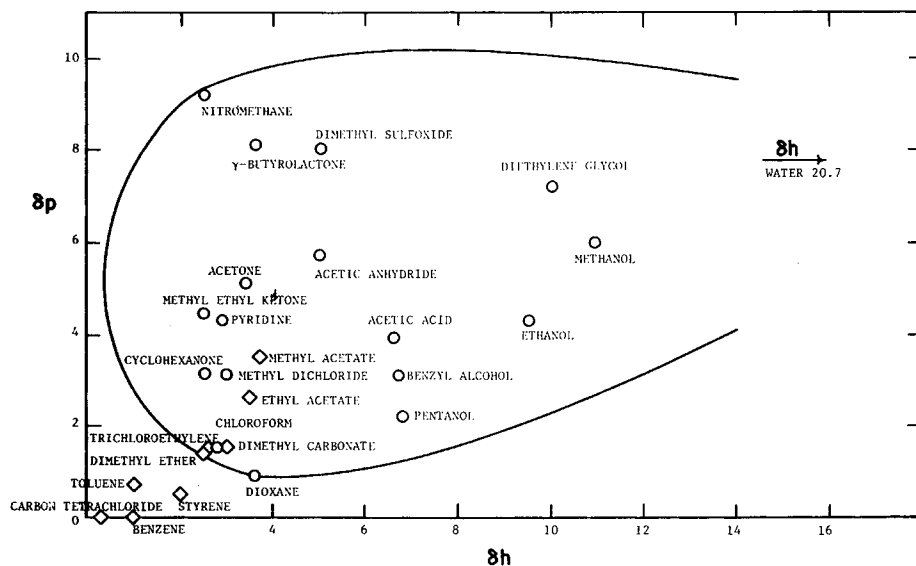
Fig. 4. Poly(vinylpyrrolidone) solubility map: (O) soluble; (◊) insoluble.
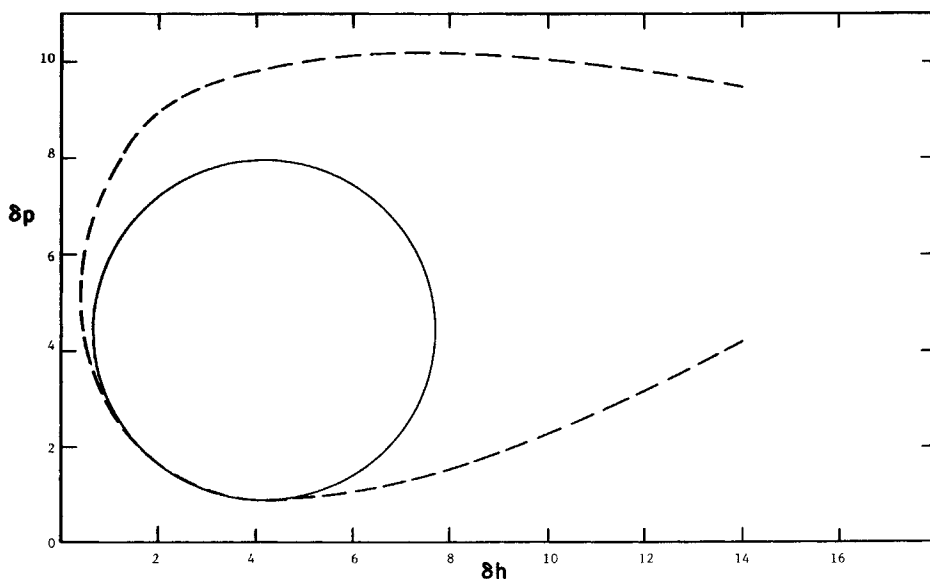

Fig. 5. Map showing overlap of polysulfone and poly(vinylpyrrolidone) solubility parameters.

the spinning solution which gel into the solid phase in the quenching process, e.g., polysulfone and PVP. On the other hand, addition of PEG, for example, to the spinning solution is not included in this term.

Spinning Solution Composition and Hydraulic Permeability

It was found that the use of lower molecular weight PVP produces higher L_ps. Some representative results are shown in Table II. The observed increase in L_p is greater than would be anticipated from the viscosity decrease.

TABLE II
Effect of PVP Molecular Weight on Fiber Properties

Fiber designation	Poly-sulfone, wt-%	PVP, wt-%	Molecular weight of PVP	Viscosity, cP	Physical properties		
					$L_p \times 10^5$, cm/sec-atm	Initial modulus, kg/cm^2	Tensile strength, kg/cm^2
II-1	26	15	40,000	18,000	12.6	850	59.9
II-2	26	15	10,000	13,000	63.0	1265	96.4
II-3	35	0	—	11,000	2.2	3160	163.5

The data indicate that the physical properties of sample II-2 compared to those of sample II-1 are also improved. It is not possible from these limited data to delineate the causes of the differences in fiber properties. The complexity of such comparisons is further illustrated with sample II-3, which does not contain PVP. High initial modulus and tensile strength, which can be attributed to the higher polysulfone content, are observed. The fiber displays very low L_p inspite of the low viscosity of the spinning solution. (A viscosity of at least 10,000 Cp was found to be desirable for continuous production. Therefore, the polymer concentration of this solution was increased to yield this viscosity). The relationship between the solution viscosities and the total dissolved polymers is shown in Figure 6.

Increasing the polymer content in the spinning mixture directly decreases the hydraulic permeability of the fibers, as shown in Figure 7. The effect of spinning conditions and solution compositions is further illustrated in Table III.

The substitution of PVP for polysulfone in the solution, as illustrated by
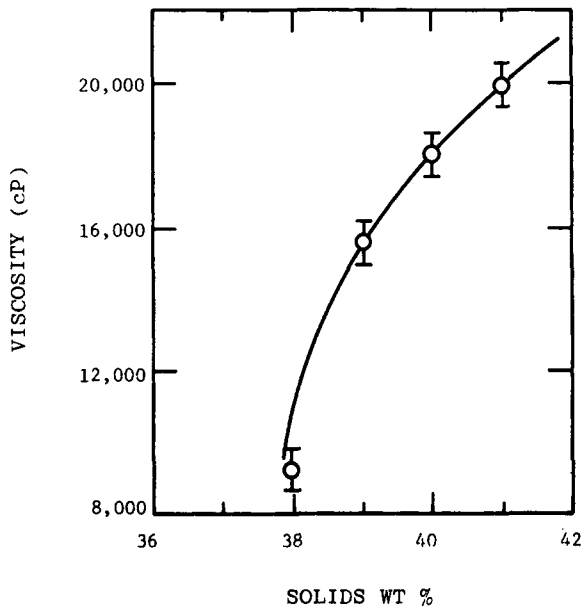

Fig. 6. Viscosity (50°C) vs. solids in the spinning mixture. The PVP fraction remained constant while the polysulfone fraction was increased.
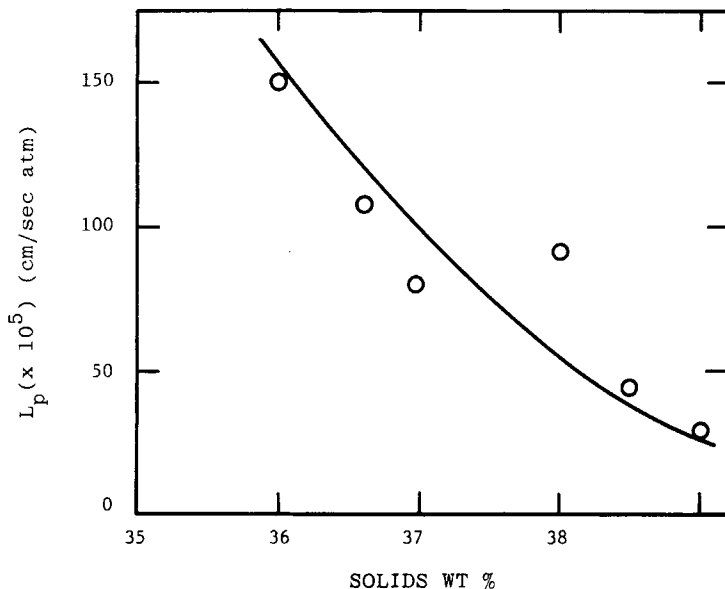
Fig. 7. Relationship between amount of polysulfone in solution and hydraulic permeability. The fraction of the PVP was kept constant.

samples III-2 and III-3, produces a much more permeable fiber. It is not possible to make this substitution on a one-for-one basis since a larger change in viscosity occurs per unit change of polysulfone than occurs with PVP. Table III also reflects the influence of the differences of the inside quench fluids that were used to produce these fibers. As the polymer content and/or viscosity increases, it is necessary to slow down the internal quench rate so that adequate draw-down can be achieved to yield fibers with equivalent dimensions.

An interaction between the quench conditions and other spinning parameters is expected. However, the changes in fiber properties that can be directly attributed to the internal quench are much smaller than those observed to result from changing the spinning formulation. This is also illustrated in Table IV. The quench conditions can drastically change the gross morphology of the fiber. The fact that these structural alterations do not manifest themselves in a corresponding change in permeability, as shown in Table IV, may indicate that the spun fibers have an asymmetric structure.[9]

In summary, these process variables and their relation to the hydraulic permeability indicate the following:

1. As the total fraction of polysulfone in the spinning solution is increased, there is a corresponding decrease in the hydraulic permeability.

2. There is an increase in the hydraulic permeability when the fraction of PVP is increased.

3. There is an apparent increase in both the hydraulic permeability and the mechanical properties of the hollow fiber as the molecular weight of the PVP is decreased.

4. The spinning formulation has a more pronounced effect on the hydraulic permeability than do the quench conditions.

TABLE III
Effect of Percentage of Solids in Spinning Mixture on Fiber Properties

Fiber designation	Total solids, wt-%	PVP/PS, w/w	Internal quench fluid	Viscosity of spinning solution, cP	$L_p \times 10^5$, cm/sec-atm
III-1	24	0	1:1 DMA:H_2O	1,970	46.6
III-2	35	0	4:1 DMA:H_2O	11,100	4.3
III-3	38	0.65	3:1 DMA:H_2O	9,200	150.3
III-4	41	0.57	4:1 DMA:H_2O	16,500	57.7
III-5	51	0.41	1:1 DMA:isopropanol	280,000	6.7

TABLE IV
Effect of Internal Quench on Hydraulic Permeability

Fiber designation	Solids, wt-%	Viscosity of casting solution, cP	Internal quench medium	Temp., °C	$L_p \times 10^5$, cm/sec-atm
IV-1	51	280,000	air	35	1.0
IV-2	51	280,000	1:1 DMA: isopropanol	51	6.7
IV-3	35	11,100	isopropanol	40	2.2
IV-4	35	11,100	4:1 DMA:H_2O	40	4.3
IV-5	35	11,100	air	32	3.0

Figure 8 shows the relationship between maximum pore size and the polymer content of the spinning solution. These data represent differing spinning conditions in order to keep the fiber dimensions within the target range, but illustrate the most significant variable used to control porosity. The higher solids content causes more rapid precipitation and gelation, which leads to "finer" pore texture. A direct result of this reduction in pore size is a reduction in L_p. This is not a one-to-one relationship, since a plot of pore size versus L_p is not necessarily linear. A number of variables affect the latter relationship: (1) the fiber wall thickness; (2) the distribution of pore sizes; (3) the fraction of "open-celled" pores.[9]

Figures 7 and 8 and Table III show that a reduction in maximum pore size is generally accompanied by a reduction in hydraulic permeability, although the exact trade-off is a function of many factors, sometimes quite independent of the solids content of the extrusion solution. From the morphologic analysis of the PSHF we know[9] that in most cases the fibers have an asymmetric wall and that the cross section is not completely uniform. Thus, the L_p-versus-diameter relationship is valid only for a given type of spinning process. The PSHF porosity has been studied extensively and is reported elsewhere.[9]

Effect of Spinning Variables on the Dimension of PSHF

Some of the variables that directly influence the dimension of the extruded fiber are correlated with the spinning operation. For example, the effect of extrusion rate is illustrated in Figure 9.

The jet temperature controls the viscosity of the extrudate at a given com-
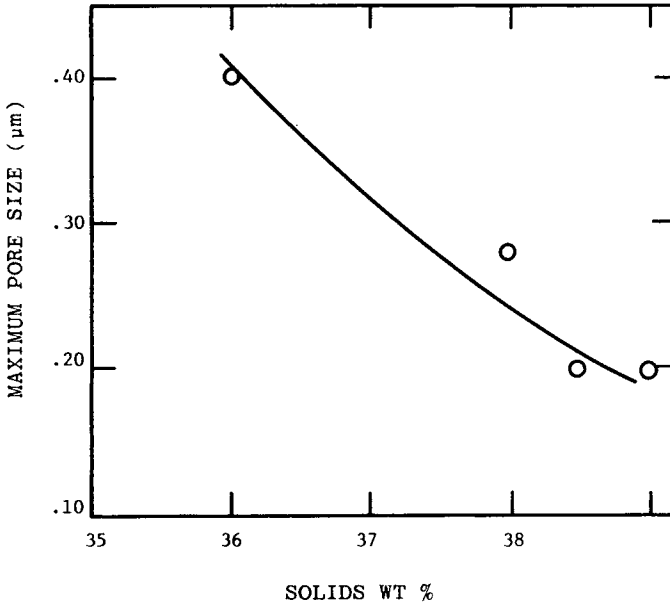
Fig. 8. Relationship between maximum pore size and solids content (constant fraction of PVP in solutions).
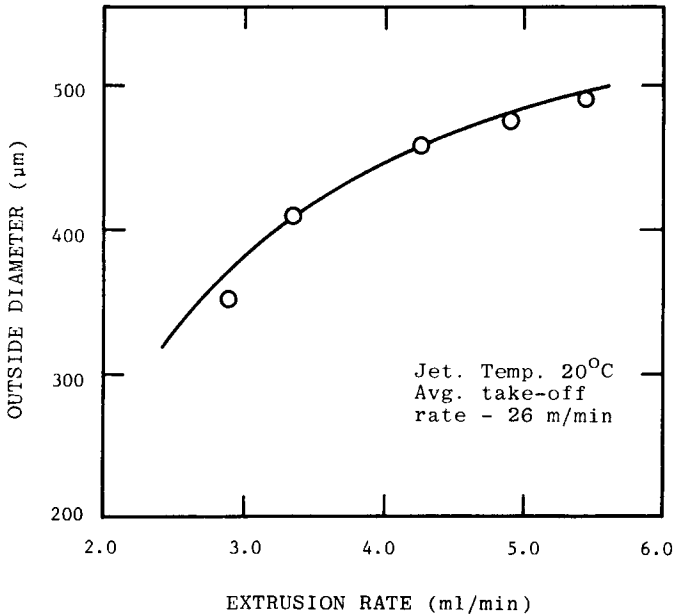

Fig. 9. Relationship between outside diameter (OD) and extrusion rate.

position; this, in turn, determines the response of fiber dimension to pull-off rate. Alterations in viscosity (through solids content or temperature) or alterations in the jet orifice sizes shift the response profile, but the general conclusions are still valid.

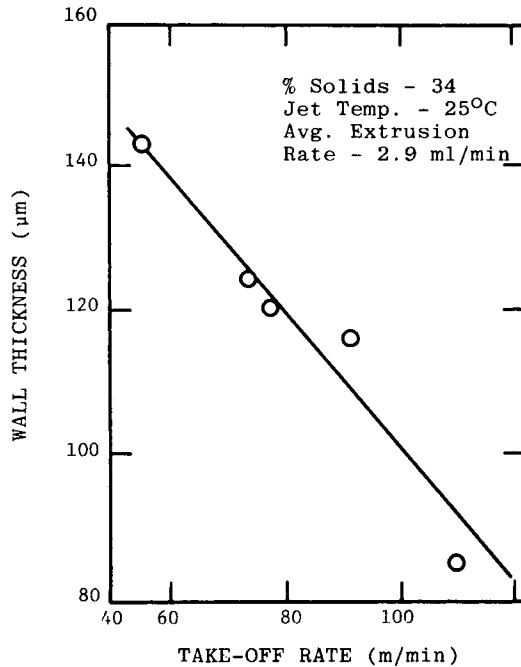As extrusion rate is increased, the outside diameter also increases if the

Fig. 10. Effect of take-off rate on wall thickness.

take-off rate is maintained constant. The relationship is not linear because some of the increase in the polymer content is assimilated into a thicker wall section. At each take-off rate, a congruent graph would be expected.

Figure 10 illustrates the effect of take-off rate on the wall thickness, at a constant extrusion rate and jet temperature. With a fixed delivery of polymer, the increased take-off rate leads to a draw-down of wall thickness and a very small change in inside diameter (ID). Similarly to the relationship plotted in Figure 9 for outside diameter and wall thickness, the relationship between wall thickness and take-off rate would be expected to shift upward if the extrusion rate were higher.

Effect of Spinning Process Variables on Mechanical Properties

A high initial modulus is required by fibers that must withstand high hydraulic pressures. For long-term usage, elastic failure is the major failure mode to be guarded against. The formulation, given in eq. (1), based on an elastic failure mode, conservatively estimates the failure pressure.

In Figure 11, the relationship between the solids content of the extrusion solution and the initial modulus measured in tension is shown.

The tensile strengths of fibers spun with an average *OD/ID* (outside diameter/inside diameter) of 3/1 ranged from ~500 kg/cm^2 to ~80 kg/cm^2. The higher values were obtained when only polysulfone was present in the spinning solution, and the lower values were obtained with increasing fractions of PVP in the mix. The mechanical properties of the fiber vary according to whether it is wet or dry. Since the fibers are used wet for reverse osmosis or ultrafiltration, it is necessary to consider the mechanical properties in the wet
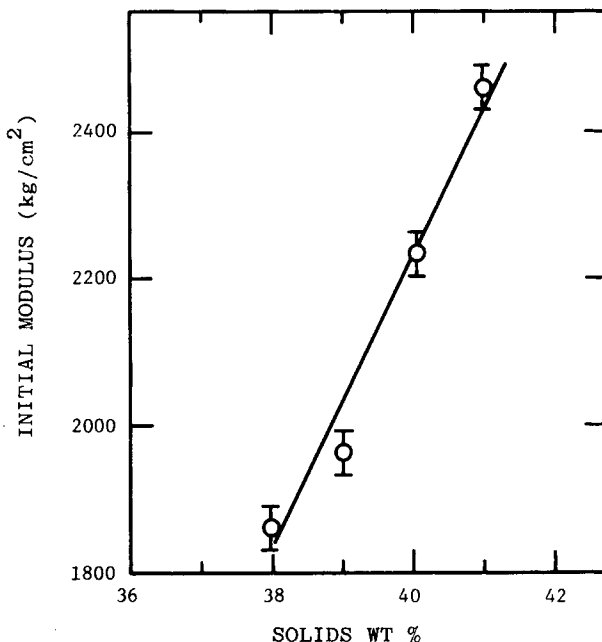
Fig. 11. Relationship between solids content (wt-%) and initial modulus. The PVP fraction remained constant while the polysulfone fraction was increased.

state. A minimum of seven days is sometimes required for a dried fiber to reequilibrate in water and to gain a constant L_p. The mechanical properties of the PSHF in the wet and dry states are compared in Table V. These fibers show mechanical properties which are projected to be sufficient for performance under high-pressure reverse osmosis conditions. The differences in mechanical response between the wet and dry states are expected. Dense polysulfone is a hydrophobic polymer which can dissolve less than 0.5 wt-% water. However, the wettability of a porous fiber is also a function of its ability to absorb the water into its pores. Thus, two parameters are involved rewetting porous fibers: (1) the equilibrium water content of the polymeric matrix, and (2) the morphology and wettability of the fiber pores. The first is influenced by the traces of PVP and other additives which remain in the quenched polymers and as such plasticize the wet fiber. The second depends upon the dimensions of the pores and on the addition of surfactants to the quench bath or to the stored fibers. Differences in the wet and dry elongation properties were observed in several cases, even when polysulfone hollow fibers were spun without PVP. For example, polysulfone spun with an OD/ID of 4.7/0.81 displays an average wet elongation of 48% and a dry elongation of 38%. This difference reflects the morphologic changes caused by the drying effect.

The use of different quench media on the internal and external surfaces makes it possible to spin fibers with a wide choice of different morphologic structures. However, the modifications in the quench media can have a marked influence on the mechanical properties of the fibers. For example, a sharp increase in the quench rate, caused by the infusion of a strong nonsolvent (isopropranol), produces a highly brittle fiber with a maximum elonga-

TABLE V
Mechanical Properties of PSHF in Wet and Dry State (OD/ID 3:1)

PSHF designation	Tensile strength, kg/cm^2		Elongation, %		Modulus, kg/cm^2		Critical pressure P^e, psi[a]		Storage materials, wt-%	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry		
V-1	323	338	76	36	2335	2660	2360	2685	95(isopropanol)	5(Triton)
V-2	278	328	76	58	2010	2465	2030	2090	95(H$_2$O)	5(Triton)
V-3	336	368	52	34	2255	2785	2525	3220	95(MeOH)	5(Na dodecyl) sulfate
V-4	299	283	49	51	2535	2250	2725	2420	60(H$_2$O)	35(glycerin) 5(Triton)
V-5	363	405	42	27	3165	3730	3405	4010	95(isopropanol)	5(Triton)

[a] Calculated according to eq. (1).

TABLE VI
PSHF Properties versus Dimensions ($t/\overline{OD}$)

PSHF designations	Wall thickness/ outside diameter $t/\overline{OD}$	Calculated collapse pressure P^e, psi	Maximum pore diameter cm × 10^4	L_p × 10^5, cm sec^{-1} atm^{-1}
VI-3	0.258	1108	0.37	46
VI-4	0.260	1322	0.26	21
VI-6	0.269	1380	0.34	59
VI-7	0.269	1230	0.44	85
VI-9	0.276	1910	0.24	48
VI-12	0.295	1625	0.25	42
VI-14	0.298	1600	0.32	81
VI-16	0.310	1975	0.23	71
VI-19	0.333	2060	0.18	59
VI-20	0.337	2415	0.18	150
VI-21	0.342	2315	0.18	102

tion of 8% (compared to 50% when quenched from 3/1 DMA/water). Air was found to be the slowest internal quench medium; it is useful with solutions with viscosities of 50,000 cP and up. Some technical difficulties are encountered when air is employed for low viscosity spinning solutions.

Several external quench formulas have been investigated. All of these external solutions followed an initial external air quenching. Quenching with 1/1 DMA/water or isopropanol has not shown any improved mechanical properties compared to water quenching. However, the introduction of surfactants to the water has been shown to affect the ability to rewet dried PSHF.[9]

In Table VI are listed, in descending order of $t/\overline{OD}$, a representative set of fiber properties. The calculated critical pressure, based on eq. (1), generally increases with an increase in $t/\overline{OD}$ as would be expected. However, the influence of modulus is seen clearly when we compare, for example, the P^e of VI-9 to VI-16. In this example, failure pressures in the range of 1900 psi are projected for fibers having $t/\overline{OD}$ of 0.276, as well as those having the higher $t/\overline{OD}$
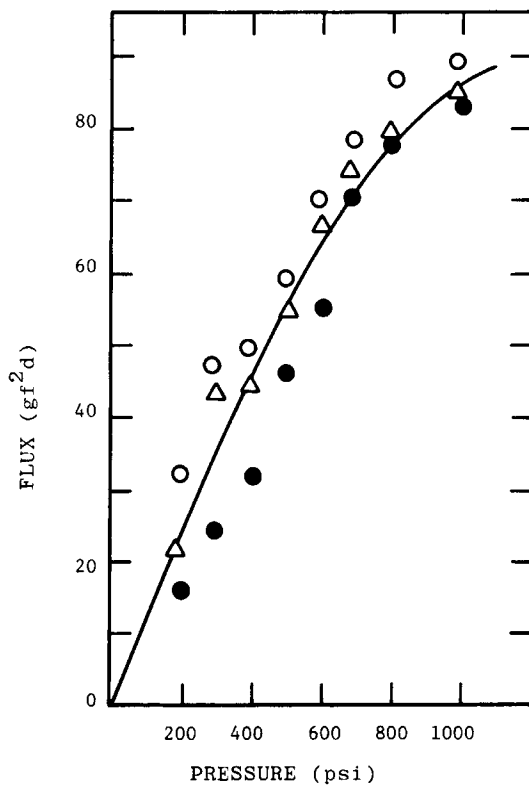
Fig. 12. Flux vs. pressure for three bundles of uncoated polysulfone hollow fibers under elevated hydraulic pressure. Each bundle contains 100 fibers; fiber wall = 100 μm; internal diameter = 100 μm; $t/\overline{OD}$ = 0.3; L_p = 47 $\times$ 10^{-5} cm/sec-atm.

of 0.310 even though the maximum pore sizes are equal. The factors which are not considered in Table VI are the degree of porosity and the total void volume which influence both the modulus and the hydraulic permeability. (In the above case, VI-9 was quenched to have a denser structure.) These morphology factors are discussed in detail elsewhere.[9,10]

The rate at which the fiber solidifies has a direct influence on its modulus. For example, the internal quench rate can be controlled by inserting different proportions of DMA/water in the quench. The use of a 1/1 mixture gives a relatively quick, uniform quench. However, slowing of the quenching rate by using 3/1 DMA/water in the inside core generally produces a fiber with better mechanical properties. This can be seen by comparing samples VI-20 and VI-21 (Table VI), which were spun in the same run with identical conditions but with a 3/1 quench composition for the first and 1/1 for the second.

Hydraulic Pressure Response of Polysulfone Hollow Fibers

The response of water flux to hydraulic pressure is shown in Figure 12. For most of the spun fibers calculated, critical pressure ranges from 1000 to 3000 psi.

In Figure 12, a characteristic linear increase in flux with increase in pres-

sure is shown up to 800 psi. A nonlinear relationship is observed for higher pressures. The fiber shown has a calculated critical pressure of 1800 psi. Some PSHF which have P^e values of over 2000 psi show linear relationships up to 1400 psi. In most cases, no disastrous collapse of fiber under the hydraulic pressure was observed. The nonlinear portion of the flux curves can be attributed to four cases: (1) collapse of some fibers in the bundle, (2) compaction of the external fiber microstructure, (3) collapse (pinching) of fibers near the potted ends of the bundles by deformation of the potting resin, and (4) plugging of the fiber pores by dispersed solids in the water.

The following elaborates on these points. The collapse of fibers is attributed mainly to defects in the fiber walls. The introduction of voids or intrusions in the walls can produce weak spots which would compact under pressure.

It is known that the flat polysulfone porous membranes are compressed to a certiin extent under hydraulic pressure[10] and that this compression results in a decline in the water flux. Some of the polysulfone hollow fibers that were spun have asymmetric structures in which the internal fiber wall is the dense portion of the structure.[9] Such a fiber undergoes compaction at the external surface without a total collapse of the fiber.

Our observations have shown that the weakest part of the fiber bundle is near the potting ends. Potting materials often change the nature of the fiber upon contact. Some of them (epoxies) cause the fiber to be rigid and fragile, and others (polyurethanes) soften it. Most of the testing problems of the high-pressure experiments occur in these areas of the bundles.

In the experimental measurement of flux versus pressure, the ultrafiltration of high molecular weight species which are suspended in water occurred. The application of high hydraulic pressure forced these species into the fine porous structure of the fibers, thus decreasing the fiber's transport properties.

CONCLUSIONS

This study has shown that polysulfone hollow fibers that withstand high hydraulic pressure can be successfully spun by the dry–wet spinning process. The many variables that are involved in such a spinning process make it difficult to recommend any single "best" spinning process. Rather, they permit preparation of a wide range of PSHF with diverse properties. This paper deals only with relationships between properties and extrusion conditions. More detailed analyses of fiber morphology are presented in a subsequent paper.

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