Improved Spinnerette Design for Extrusion of Polymeric Large Internal Diameter Hollow Fiber Membranes

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ABSTRACT: Spinnerettes for extrusion of large (~ 1 mm) internal diameter (i.d.) hollow fiber membranes must possess certain features to extrude fibers with the proper tensile and geometrical properties. Spinnerette designs that properly extrude small i.d. (< 200 μm) hollow fibers will produce large i.d. hollow fibers with low burst strengths because of poor flow patterns and insufficient time in the spinnerette to knit a strong seam interface. In this report, an alternative design is offered that provides much better fiber properties without creating high pressure drops or shear stresses at the spinnerette wall that would normally result in melt fracture. The equations that guide the presented spinnerette design are provided and the suggested design is successfully guided by the results. The new spinnerette design also has the feature of allowing rapid change of hollow fiber wall thickness by making the core fluid pin replaceable. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2157–2163, 2002

Key words: membranes; hollow fiber; spinnerette; extrusion; microfiltration

INTRODUCTION

Extrusion of polymeric hollow fibers is an established technology practiced widely throughout the plastics industry. However, problems are often encountered when practitioners must extrude large internal diameter (i.d.) hollow fibers with narrow tube walls. These problems show up in the final product performance in misshapen tubes, or tubes with low burst pressure. We have found these problems to be particularly evident when attempting to extrude polymer solutions for membranes. This application has particular difficulty because the polymer must flow around internal structures within the spinnerette and re-meld to form a nearly seamless tube. The complications arise because polymer solutions for membranes are often complex blends including more than one polymer. The effect of the mixture is to provide competition for surface sites, lessening the opportunity for the desired membrane polymer to form a strong interface at the seam.[1] This effect is exacerbated by the tendency of relatively low molecular weight solvents to preferentially occupy the surface as the polymer blend is sheared going through the spinnerette channel. This tendency stems from the property of the lowest viscosity material to concentrate at the locus of highest shear.[2]

Superficially, there are many similarities in spinning small and large i.d. hollow fibers, but stable and continuous extrusion in each case requires many important process modifications. For example, we have found that spinnerettes designed for extrusion of small i.d. hollow fibers are unsatisfactory for producing large i.d. hollow fibers for polymeric membranes. Large i.d. hollow fibers produced from such spinnerettes are se-

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verely eccentric and possess low burst pressures. These problems were evident in the case of both melt-processed and solution-processed polymer blends. This report presents a design for large i.d. hollow fibers that have particular application to the fabrication of polymeric membranes. Membranes from the presented design show excellent centricity and very high burst pressures compared with those produced by a conventional design. The presented design also provides unusual flexibility to alter the tube wall thickness without requiring the construction of a new spinnerette body. Flexible construction has not been normally practiced as far as we can discern. A cursory search of the patent literature found one reference for a flexible film die design with removable inserts.[3] Although practitioners may be designing spinnerettes with the ability to rapidly alter tube dimensions, we have not found any literature to support this possibility. Thus, the current work may be the first published example of a hollow fiber spinnerette with removable inserts.

EXPERIMENTAL

Melt-spun polymeric blend hollow fibers were extruded on an apparatus and method that are described in detail elsewhere.[4] Briefly, fibers were extruded on a $\frac{3}{4}$-in. Killion (Orange Grove, NJ) single screw extruder with a 0.58 cc/rpm Zenith gear pump. The spin pack was fitted with a Memtec 11X stainless steel fritted pleat filter (7 μm discrimination). Solution spun hollow fibers were extruded on a homemade melt pot extruder with a 0.58 cc/rpm Zenith gear pump. N_2 pressure above the melt pot was maintained at 10 psi to assure a steady flow of polymer solution to the gear pump. Melt spun polymer blends were poly(ether ether ketone) (PEEK; Victrex, NJ), poly(phenylene sulfide) (PPS; Amoco, Alpharetta, GA), and syndiotactic polystyrene (SPS; Dow, Midland, MI). Blend details can be found elsewhere.[5,6] All of these materials demonstrated identical performance in these tests with respect to hollow fiber extrusion as a function of spinnerette design. Similarly, solution spun fibers from blends of polysulfone (Amoco, Alpharetta, GA), blended with 1-methyl-2-pyrrolidinone, isopropylalcohol, and polyvinylpyrrolidone (PvP), with a core liquid of PvP, IPA, and water, also showed spinnerette-dependent performance identical to that of the melt-spun polymers. That is, in all cases, large i.d. hollow fibers extruded through a spinnerette "scaled-up" from a small i.d. hollow fiber design were misshapen with obvious seams and low burst pressures. Membrane burst pressures were tested using an apparatus described in detail elsewhere.[4] Fiber burst was obtained by wetting the fibers with ethanol, followed by a solvent exchange with water, and then performing a standard bubble point test.[7] Fiber blow-out can be easily observed as a rapid expulsion of air from the testing beaker unit. The location of the burst is determined by observation of bubbles emanating from the submerged fibers.

Table I Glossary of Terms and Symbols used in Model Calculations

Variable	Meaning	Unit
L	Flow length in annulus	inches
H	Annular width	inches
R_0	Outside radius of bore	inches
R_i	Outside radius of pin	inches
R	Mean radius	inches
K	Die conductance	in.^{3}
k	Ratio R_i/R_0	—
ΔP	Pressure drop	psi
$\tau\omega$	Shear stress at wall	psi
V	Volumetric flow rate	in.^{3}/s
T_{res}	Residence time	s
Q	Velocity	in./min
η	Viscosity of polymer	lb-s/in.^{2}
$\gamma\omega$	Shear rate at wall	s^{-1}

Calculation of spinnerette flow properties was performed on a commercial spreadsheet program. A glossary of terms and symbols used in model calculations is given in Table I. Spinnerette design was performed using Autocad (Autodesk Inc., Sausilito, CA). Spinnerettes were fabricated at Petersen Instruments (Concord, CA).

The equations for flow through channels including the annular slits capable of producing hollow fibers have been derived by Michaeli[8] and others.[9] The calculations were solved from the equation set that involves four simplifying assumptions: (1) polymer blend flow is laminar; (2) polymer blend flow is Newtonian, that is

$$\tau = \eta\gamma \tag{1}$$

(3) polymer blend adheres to the walls of channels it flows through; and (4) the system is isothermal.

The pressure drop is related to the volumetric flow rate and the viscosity by eq. 2:

$$V = (K/\eta)\Delta P \quad (2)$$

Pressure drop is an important consideration in spinnerette design because it can have such a large effect on the rheology and flow properties of the extruding polymer, as seen by the relationships in eq. 2. For non-Newtonian fluids, pressure drop can be utilized to reduce the viscosity of a shear thinning fluid; however; in general it is most convenient to not have a very high pressure drop in the spinnerette channels. High pressure drops are often associated with large die swells and poor polymer flow stability. In eq.2, K is the die conductance, which is a function of the flow channel geometry. For a circular channel with a length-to-radius ration $\gg 1$, the die conductance is defined as

$$K = (\pi R^4/8L) \quad (3)$$

In contrast, for a circular slit (from which emerges a hollow fiber), K is defined as

$$K = (\pi R^4/8L)[(1 - k^4) - (1 - k^2)^2/\ln(1/k)] \quad (4)$$

where k is the ratio of the inside annular radius to the outside annular radius:

$$k = R_i/R_0 \quad (5)$$

In these separate cases of a circular channel and a circular slit, eqs. 3 or 4 can then be substituted into eq. 2 to obtain the pressure drop for the spinnerette as a function of polymer blend viscosity and volumetric flow rate. For the special case where the polymer flow is divided into a number of channels, the total flow is divided by the number of holes through the pin (n). In this case, eq. 3 can be rewritten as

$$\Delta P = (\eta V)/(Kn) \quad (6)$$

A second important criterion in the design of polymer dies concerns the shear stress at the wall of the flow channel. The shear stress at the wall should in practice be minimized to mitigate the phenomenon of melt fracture. The actual shear stress above which melt fracture will be observed is a complicated function of many chemical and engineering factors;[10–12] however, it is a rule of thumb that wall shear stresses should be on the order of 10 psi or less to prevent melt fracture.[13]

For flow through a circular channel, the shear stress at any radius is

$$\tau = (\Delta P/2L)r \quad (7)$$

In contrast, shear stress at the wall where $r = R$ is

$$\tau_\omega = (\Delta P/2L)R \quad (8)$$

For a circular slit, the shear stress at any radius, r, is

$$\tau = (R\Delta P/2L)[(r/R) - ((1 - k^2)/(2\ln(1/k))(r/R)] \quad (9)$$

At the wall, eq. 9 for shear stress reduces to eq. 10, where H is the width of the annulus:

$$\tau_\omega = (\Delta P/2L)H \quad (10)$$

Finally, the residence time in a section is inversely proportional to the mean velocity, which for a circular section is

$$T_{\text{res}} = L/Q \quad (11)$$

and for an annular section is

$$T_{\text{res}} = (8\eta L^2/R^2\Delta P)[(1 - k^4)/(1 - k^2) - (1 - k^2)/\ln(1/k)]^{-1} \quad (12)$$

RESULTS AND DISCUSSION

When a tube of melted or solvated polymer blend exits an annular slit, the tendency is for the tube to collapse as the material draws. To maintain the geometry of the extruding tube, it is necessary to flow a core gas or fluid down the center (referred to as the lumen) of the tube. The spinnerette is the usual place to make the modification to allow the core fluid to enter the polymer flow channel. In Figure 1 is a drawing of a spinnerette design from a successful small hollow fiber design adapted to produce a large i.d. hollow fiber. In this case, the molten polymer enters through the top face and flows around the center pin through which flows the core liquid that enters through a stainless steel side port. With this design, the polymer must flow around the core fluid pin and re-meld while transiting a relatively small dis-

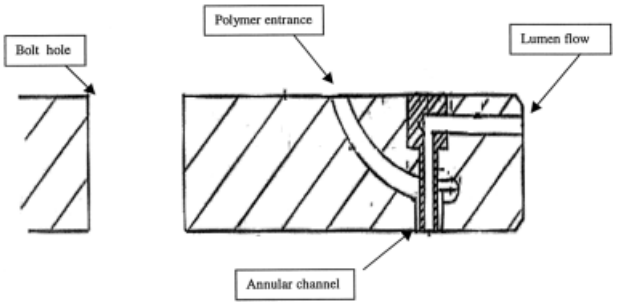

Figure 1 Basic design of a successful small i.d. hollow fiber spinnerette.

tance prior to exiting the spinnerette. A scanning electron micrograph (SEM) of a PPS hollow fiber produced by this spinnerette is presented in Figure 2. The point at which the polymer melt entered the annular channel is evident by a distinct thickening in the fiber wall. The fiber wall gets progressively narrower, and a seam is obvious where the polymer did not meld. Fibers with an appearance like this typically had burst strengths at transmembrane pressures of $\leq$10 psi. In those cases where the polymer blend was particularly viscous or had a particularly low concentration of polymer, the fiber would split in the solvent leaching step. It is interesting to note that this design had previously been used successfully in the production of cellulose and polycarbonate membranes with membrane diameters between 100 and 200 μm, having burst pressures $>$ 10 bar.

Design of a successor spinnerette took into account our initial observations that the problems

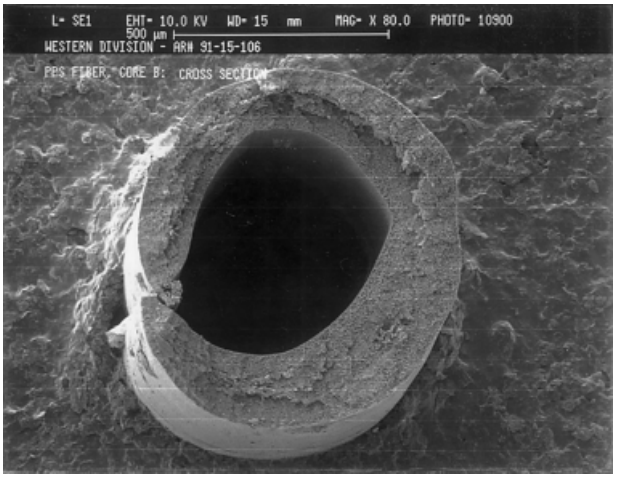

Figure 2 Scanning electron micrograph of PPS fiber produced from the spinnerette design shown in Figure 1.

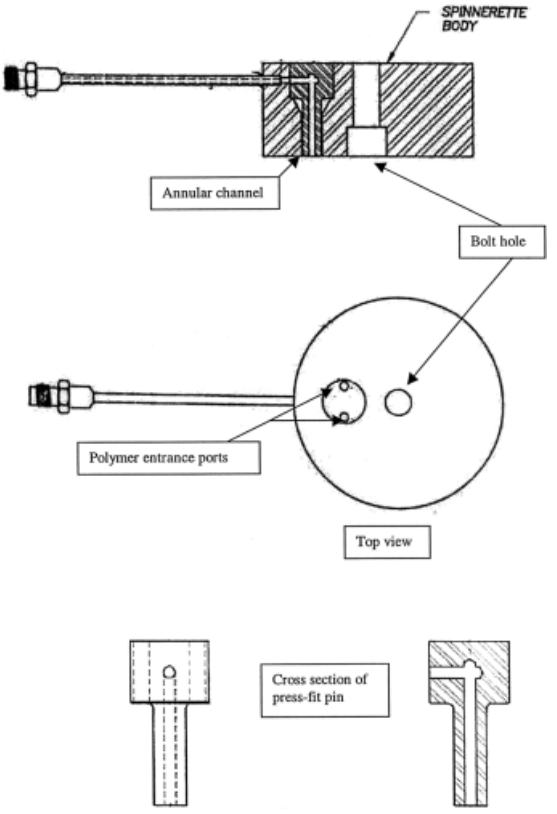

Figure 3 Design of two-channel spinnerette for extrusion of large i.d. hollow fiber membranes. The four-channel spinnerette has four circular channels and ports feeding the annular channel.

shown in Figure 2 were a result of two spinnerette features shown in Figure 1; they are (1) the polymer melt has a long path around the core fluid pin to meet itself on the opposite side from its entrance point, making it difficult to fill the flow channel, and (2) the residence time of the polymer blend in the annular flow channel is too short to allow adequate re-melding given the limitations of a low polymer concentration in the blend. The design constraints seen with small i.d. hollow fibers are a result of the necessity to minimize the flow length in the spinnerette. By inspection of eq. 3, decreasing L would be the easiest way to increase die conductance because R is by definition small. Furthermore, blends for making small i.d. hollow fiber membranes can have significantly lower viscosity because they are typically drawn to a greater degree outside of the extruder, a process that can enhance the melt strength of a polymer solution.[1,14] Figure 3 is a diagram providing the general concept of the improved design. This design shows that the polymer now enters

Table II Results using Equations for Flow Properties through a Circular Channel

Flow Property	0.05 inch Diameter	0.1 inch Diameter
Number of holes through pin (in.)	2	2
Diameter of holes through pin (in.)	0.05	0.1
Flow length through pin (in.)	0.5	0.5
Specific gravity of polymer blend (g/cc)	1.25	1.25
Viscosity (poise)	2000	2000
Flow rate of polymer through meltpump (g/min)	30	30
Length-to-diameter ratio of circular channel	10	5
Channel radius (in.)	0.025	0.05
Pressure drop through circular channel (psi)	1180	72.1
Shear stress at wall	29.5	3.6
Shear rate at wall (s^{-1})	978	124
Volumetric flow rate through one channel ($in.^3/s$)*	0.012	0.012
Velocity of melt through hole (in./min)	372	93
Residence time (s)	0.08	0.32

* Conversion of poise to (lbs · sec)/in^2: divide poise by 68,947.

the spinnerette from the top face into two channels and travels a greater distance in the annular channel prior to exiting the spinnerette. In this design, as in the design in Figure 1, the polymer blend flows through two flow channel types. In the case of the spinnerette described in Figure 3, the polymer flows through two circular channels prior to feeding the annular slit. A subsequent generation had a similar design but had the annular slit fed by four circular channels. Prior to engaging in expensive machining, the calculations described in the Experimental section were employed to make sure that the resulting spinnerette would not violate good engineering practice. The calculated results of the flow properties using the equations in the Experimental section and the specified dimensions and polymer blend properties that are typical for the application are shown in Tables II and III.

Because of the character of the flow equations, several variables have highly nonlinear relationships with other factors. The most highly sensi-

Table III Results using Equations for Flow Properties through an Annular Slit

Flow Property	0.1 inch Width	0.2 inch Width
Hole diameter (in.)	0.3	0.3
Pin outside diameter (in.)	0.28	0.26
Flow length of annular channel (in.)	0.6	0.6
Flow rate of polymer blend in annular channel (g/min)	30	30
Specific gravity of polymer blend	1.25	1.25
Measured viscosity of polymer blend (poise)	2000	2000
Viscosity (lb-s/$in.^2$)	0.029	0.029
Annular width (in.)	0.01	0.02
Length-to-slit width ratio	60	30
k	0.9333	0.8666
Pressure drop (psi)	6408	954
Shear stress at wall (psi)	53.4	15.9
Shear rate at wall (s^{-1})	1607	416
Residence time in annular section (s)	0.21	0.35

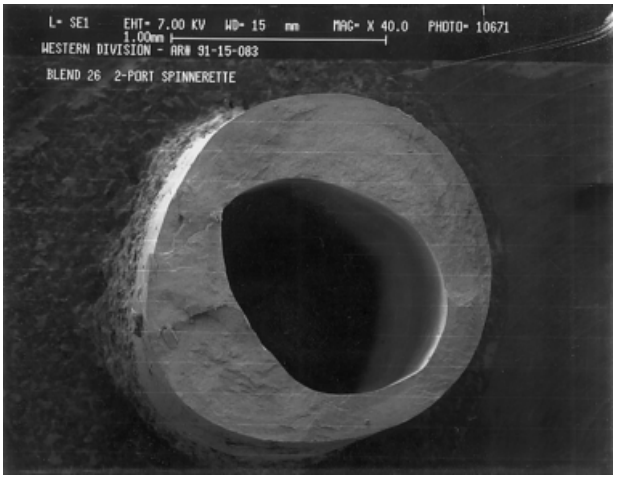

Figure 4 Hollow fiber membrane produced from two-port spinnerette using the design shown in Figure 3.

tive variable is the die conductance, which is an important design criterion because of its direct relationship to pressure drop and wall stress. For a spinnerette design as described by Figure 3, the variables R (eq.3) or k (eq. 4) are varied and the result is provided for a situation of constant polymeric flow rate. It is clearly seen that the radius of the circular channels will have a very large effect on the flow properties of the polymer blend prior to its entry into the annular section of the spinnerette. The results suggest that the diameter of the circular channels should be at least 0.1 in. A parameter we plan to vary in the design of spinnerettes, the number of channels, has a linear effect on the results because of its proportional effect on the die conductance in eq. 6. Similarly, the flow length of the circular channel has an inverse proportional effect on the flow properties by its presence in the denominator of eqs. 3 and 8.

For the annular channel, the variable k will have a very significant effect on the polymer flow properties by its effect on the die conductance (eq. 5) and by its incorporation into the pressure drop and wall shear stress calculations. The data in Table III show that the flow properties are very sensitive to the annular width. The equations suggest that a 100-μm annular width for a polymer blend with the measured viscosity shown would probably not flow through the annular section of the spinnerette because the 6400 psi pressure drop would be beyond the operating parameters for most conventional extrusion operations. The results also show that for the described configuration in Table III, the annular width should be $\sim$200 μm to bring the wall shear stress down to a level that will minimize the occurrence of melt fracture (typically $\sim$ 10 psi).

As in the case of the circular channel, the flow length of the annular channel has a proportional effect on the flow properties by its incorporation in the denominator of the calculation of die conductance (eq. 4). One of our hypotheses is that the length in the annular section should be maximized to provide maximum residence time for the re-melding of the polymer blend prior to exiting the spinnerette. The provided value of 0.6 in. in the described configuration is an estimate for the maximum length that this polymer blend can provide melt fracture-free extrusion. Although the calculated residence time in the annular section is not very long, the square dependence on the channel length indicates that this parameter can have a significant effect on the result.

Two spinnerettes were machined according to the design generically described in Figure 3: one had two circular channels feeding the annular slit (as shown in Figure 3) and the second had four such channels. Both spinnerettes had an annular channel length of 0.6 in. The PEEK hollow fibers produced by these spinnerettes are shown in Figures 4 and 5, respectively. The hollow fiber produced by the two-channel spinnerette exhibits thicker sections at the entrance points into the annular section and thinner sections at 90° to the entry points. The seam problem is greatly ameliorated, but the fiber is still misshapen. The hollow fiber produced by the four-circular channel spinnerette shown in Figure 5 has a uniform shape and no obvious thin spots, suggesting that

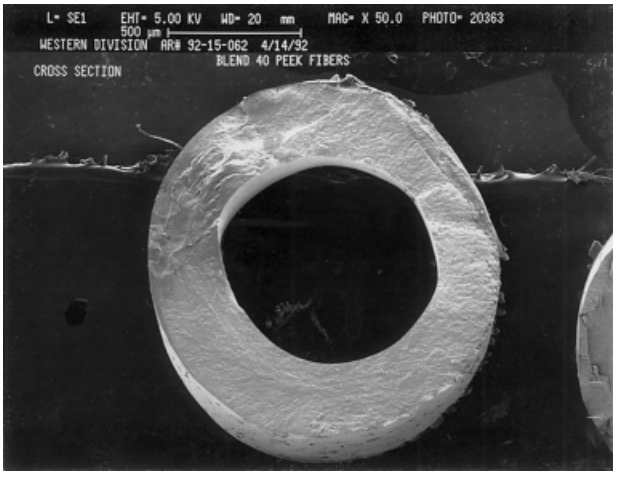

Figure 5 Hollow fiber membrane produced from four-port spinnerette using the design shown in Figure 3.

the ability to properly fill the annular channel may be an important feature of the current design. Subsequent designs making better stream lines from the polymer entry ports to the annular channels had insignificant effects on the resulting hollow fiber properties.

Another feature of the design presented here is the flexibility in changing annular widths. In the current design, the pin is press-fit into the spinnerette body and is easily removed with a press and some doweling. We have found this procedure to be executable in a matter of minutes, with no significant complications.

CONCLUSION

Extrusion of large i.d. hollow fibers for membranes requires that the polymer blend have sufficient opportunity to re-meld in the spinnerette such that the resulting fiber not have obvious seams, or be misshapen. Small i.d. hollow fiber designs simply scaled to create a larger size resulted in fiber membranes with low burst pressures due to an inability of the polymer blend to re-meld after flowing around structures within the spinnerette. We have overcome this problem by designing a spinnerette such that the time in the spinnerette is maximized and the polymer flow channels are adequately filled, thus allowing the polymer blend flows to more fully reunite, remain uniform, and not experience melt fracture. The design is simple and provides flexibility for quick alteration of the annular width.

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