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Solution-Spun Hollow Fiber Polysulfone and Polyethersulfone Ultrafiltration Membranes

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Abstract

A laboratory apparatus for making hollow fiber membranes by the solution spinning process is described. Several hollow fiber membranes from polysulfone (Udel-3500) and polyethersulfone (Victrex) polymers have been made by using the above apparatus. The effects of spin-solution composition, length of air gap, and pressure used for fiber extrusion on fiber dimensions and ultrafiltration performance of the resulting membranes have been studied and are discussed.

Key Words: Membrane; Hollow fiber; Ultrafiltration

INTRODUCTION

Polysulfone hollow fiber membranes are currently in extensive industrial use, either as such for ultrafiltration (UF) applications or as a base for subsequent coating operations for use as gas or vapor separation membranes. Open literature reports (*1–8*) on detailed and systematic studies on the cause–effect relationships on membrane making conditions and the physical dimensions and UF performance of the resulting membranes are far less extensive with respect to hollow fiber membranes compared to, for example, flat cellulose acetate membranes (*9*). The objective of this paper is twofold: to describe a simple laboratory apparatus for making solution-spun hollow fiber membranes and to illustrate the effect of membrane-making conditions on the physical dimensions and UF performance of some polysulfone (Udel-3500) and polyethersulfone (Victrex) membranes made by the above apparatus.

APPARATUS AND EXPERIMENTAL DETAILS

A laboratory apparatus for spinning hollow fiber ultrafiltration membranes has been developed by which the polymer solution can be extruded through a spinnerette as a thick hollow fiber into an air gap before immersion in a coagulation bath. A schematic diagram of the apparatus is shown in Fig. 1.

Referring to Fig. 1, the apparatus consists of a spin-solution tank (1) with a thermometer (11), an on-line filter (2), a spinnerette (3), a high pressure nitrogen cylinder (4), a vacuum pump (5), one or more outer coagulation baths (6, 7), a rotometer (8) connected to an internal gelation bath (9) provided with a funnel (10), and the necessary control (12 to 17) and safety (18) valves. Under the driving force supplied by the high pressure nitrogen, the spin-solution in the tank passes through the filter into the spinnerette, followed by the internal coagulant passing through a flowmeter. Such solution spinning is also called dry-jet wet spinning or simply wet-spinning of hollow fiber membranes in the literature, depending on the experimental conditions used.

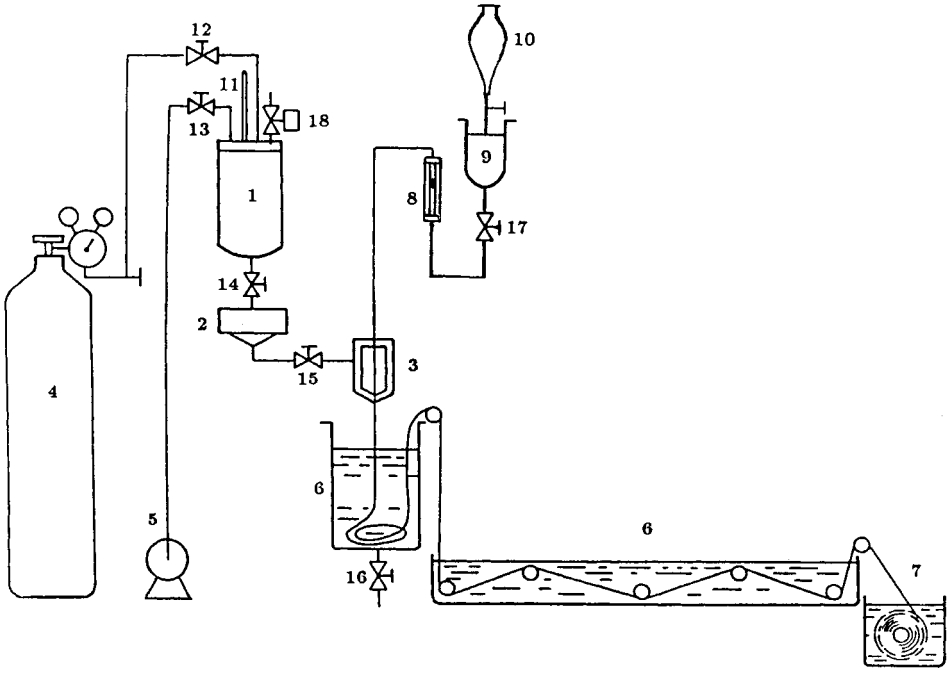

FIG. 1. Schematic diagram of the hollow fiber spin apparatus.

The spin-solution tank (~1 L in volume) is jacketed to keep the spin solution at the required temperature; the tank is also provided with a safety valve, a thermometer, and inlet connections linked to the high pressure nitrogen cylinder and the vacuum pump. The thermometer notes the temperature of the polymer solution in the tank. When the nitrogen pressure in the tank exceeds the set limit, the safety valve can exhaust the nitrogen gas automatically; nitrogen gas can also be partially exhausted by pushing the handle of the safety valve manually to adjust the pressure in the tank during the spinning process. The vacuum pump is used to get rid of gas bubbles in the polymer solution before solution spinning.

The polymer solution is filtered prior to spinning. For this purpose a 200-mesh filter disk together with a nylon or polyester fabric is used as the filtration medium. The filter disk is replaced when it becomes clogged, and the fabric is replaced every time the spin solution is changed.

The spinnerette has a tube-in-orifice form (Fig. 2), with a precision orifice containing a centrally positioned inlet tube to deliver the internal coagulation liquid. A special design ensures that the inlet tube is located in the center of the orifice. The internal coagulant is delivered through the inlet tube to create and maintain the bore structure of the fiber. The extruded fiber, after passing through an air gap, enters the outer coagulation bath. The dimensions of the resulting fiber depend on the details of spinnerette

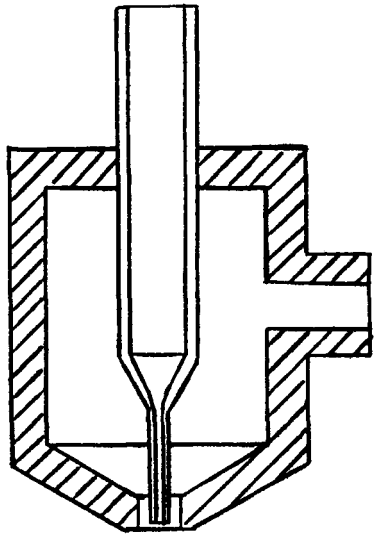

FIG. 2. Schematic diagram of the spinnerette.

design, length of air gap, fiber extrusion rate, viscosity of the polymer solution, and the nature of the internal coagulant.

The air space between the spinnerette and the external coagulant is the air gap; it can be wide open (i.e., open on all sides), or semisealed (which means partially enclosed; for example, a cylindrical chamber closed all around with open top and bottom ends). The length of the air gap is an important factor affecting the dimensions, morphology, and the performance of the hollow fiber. The length of the air gap can be changed from only a few centimeters to 200 cm in our system. With a semisealed air gap chamber, the humidity and the environment in the chamber can also be controlled.

The internal coagulant (which is water in this work) passes through a rotometer at a rate of 14 to 18 cm^3/min and flows through the spinnerette by gravity. The internal coagulant funnel is normally located 80 cm above the spinnerette; by changing this height, the pressure of the internal coagulant in the fiber bore can be changed.

After passing through the air gap, the hollow fiber enters the external coagulant bath, which is again water in this work. The fiber is subsequently forwarded through several roller guides into another water bath, where it is stored. The linear velocity of the roller varies from 1 to 8 m/min.

Spin Solution

Ultrafiltration hollow fiber membranes can be made from almost any spinnable polymer which can be dissolved in a water-soluble solvent. Generally, the spin solution consists of a polymer, additive, and solvent. The general formulations used in this work are the following: 1) polyethersulfone 200P (supplied by ICI), 17–24 wt%; polyvinylpyrrolidone (PVP, molecular weight 10K), 10–20 wt%; and *N,N*-dimethylacetamide (DMAc), 62–68 wt%; and 2) polysulfone P-3500 (supplied by Amoco), 13–22 wt%; PVP (molecular weight 10K), 10–20 wt%; and DMAc, 62–68 wt%. The spin solutions were prepared as follows: the polymer was initially dried at 110 to 120°C for 6 h in an air oven; the components were then weighed according to the chosen composition and mixed in a wide-mouth 0.5 to 1.0 L glass bottle; the bottle was kept in an air oven at 60°C for 2 days, and then the contents were roller-mixed for 2 h every day for six consecutive days. Except during mixing, the bottle was kept in the air oven at 60°C for all 6 days.

Spinning Procedure

The hollow fiber spinning procedure using the apparatus described above was as follows. Referring to Fig. 1, the spinning solution tank (1) was partially filled with the spin solution; the latter was kept at the required

temperature for 2 h before spinning; the internal gelation bath (9) and the outer gelation baths (6, 7) were filled with the selected coagulants (distilled water, in this work); the nitrogen pressure was adjusted to the required value [usually 138 to 335 kPag (20 to 50 psig), a higher viscosity spin solution would require a higher nitrogen pressure]; the valves were then opened in the order 12, 15, and 17; and the flow rate of the internal coagulant was adjusted to about 16 mL/min. The fiber would jet out of the spinnerette and be collected in baths 6 and 7.

Testing of Hollow Fibers

The outer and inner diameters of the hollow fiber were measured by using a stereomicroscope. The test system shown in Fig. 3 was used to obtain UF performance data for the hollow fibers made.

Referring to Fig. 3, the constant temperature bath 1 was used to maintain the temperature of the feed solution in tank 2 at 25°C; by using a circulating pump 3 and the adjustable valves 4 and 5, the pressure (shown by the pressure gauges 6 and 7) and the feed flow rate (shown by the rotometer 8) through the hollow fiber bundles (9) were controlled. Gauges 6 and 7 showed the inlet and outlet pressures, respectively, in the hollow fiber bundle. The permeate fluids from the hollow fiber bundles were collected in bottles (10) and analyzed.

The hollow fiber bundles were made as follows: six pieces of 30 cm length glycerol-treated fibers were collected into a bundle; the external surfaces of the two ends of the bundle were then covered with epoxy glue; each end was then potted into a ¼ in. diameter polypropylene tube of 4 cm length; after 24 h of epoxy curing, the bundle was immersed in distilled water for 12 h; the potted bundle was then assembled into the test system.

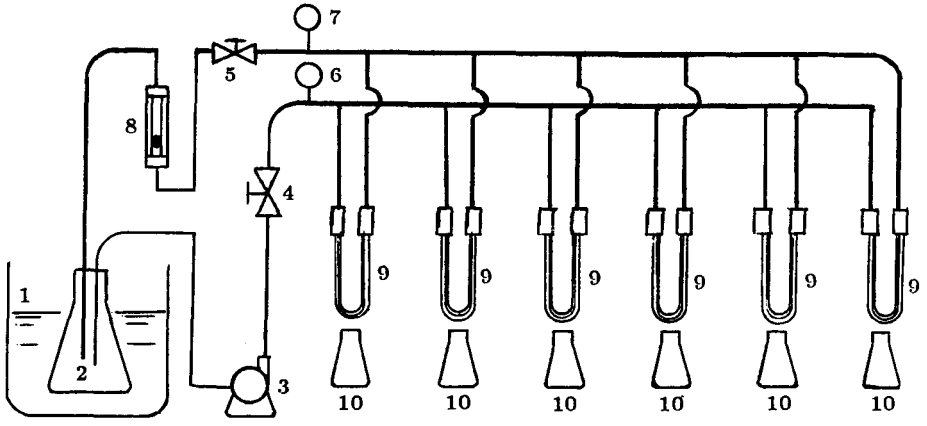

FIG. 3. Schematic diagram of hollow fiber test system.

For test purposes the feed solution was either pure water or an aqueous solution of 200 ppm polyethylene (PEG). A series of PEG solutes of different molecular weights were used as reference solutes. In each test the pure water permeation rate (PWP, in g/cm^2·h) and membrane permeate product rate (PR, in g/cm^2·h), and solute separation [defined as (solute ppm in feed − solute ppm in product)/solute ppm in feed] were determined. A Beckman (Model 915B) Total Carbon Analyzer was used to detemine the solute concentrations in the feed and product solutions. Because of the very low solute concentrations involved, the PWP and PR data were essentially identical in all the experiments reported herein, and hence the PWP data alone are reported here.

RESULTS AND DISCUSSION

Effect of Spin Solution Composition on Resulting Fiber Dimensions and Membrane Performance

Table 1 gives data on the effect of spin-solution composition for six membranes made under identical spinning conditions on the resulting fiber

TABLE 1
Effect of Spin-Solution Composition on Membrane Performance[a,b]

	Hollow fiber no.					
	S_1	S_2	S_3	S_4	S_5	S_6
Spin solution (wt%):						
Polyethersulfone	20	20	22	22	0	0
Polysulfone	0	0	0	0	21	17
PVP	4	10	4.4	11	10	17
DMAc	76	70	73.6	67	69	66
Membrane performance:						
PWP (g/cm^2·h)	0.88	4.53	1.90	1.94	1.39	7.90
Solute separation, %:						
PEG-6000	78.3	68.3	86.1	77.3	89.0	71.1
PEG-9000	94.4	84.7	94.9	92.9	92.8	90.5
Fiber dimensions (mm):						
Outside diameter (o.d.)	1.410	1.510	1.280	1.470	1.453	1.350
Inside diameter (i.d.)	0.980	0.930	0.840	0.790	0.885	0.882
o.d./i.d.	1.440	1.620	1.520	1.860	1.640	1.530

[a]Spinning conditions. Temperature of spin solution: 25°C. Length of air gap: 80 cm. Internal coagulant: water at 25°C. External coagulant: water at 17°C. Nitrogen pressure: 276 kPag (40 psig).

[b]Test conditions. Pressure: 138 kPag (20 psig). Temperature: 25°C. Feed flow rate: 0.8 m/s.

dimensions and membrane performance in terms of PWP and separations of PEG solutes (MW 6000 and 9000) under identical test conditions.

Referring to PES membranes, an increase in PVP additive in the spin solution increases o.d., decreases i.d., increases the o.d./i.d. ratio, decreases solute separation, and increases PWP, indicating a bigger average pore size on the bore surface of the membrane and asymmetry in the porous structure. An increase in polymer concentration in the spin solution tends to decrease o.d., decrease i.d., increases the o.d./i.d. ratio, increases solute separation, and increases or decreases PWP, since the latter is a function of both pore size and effective thickness of the fiber wall.

Referring to PS membranes, an increase in PVP additive in the spin solution tends to decrease o.d., decreases the o.d./i.d. ratio (while the i.d. remains essentially unaffected), decreases solute separation, and increases PWP. On the other hand, an increase in polymer concentration tends to increase o.d., increases the o.d./i.d. ratio (while the i.d. remains essentially unaffected), increases solute separation, and decreases PWP. The differences in morphology between the PES and PS membranes probably arise from the kinetics of solvent exchange during the process of membrane formation.

Effect of Length of Air Gap on Hollow Fiber Dimensions

Table 2 gives data on the effect of length (L) of air gap on the resulting hollow fiber dimensions, and Figs. 4 and 5 show the effect of L on membrane performance in term of PWP and separation of PEG solutes in the molecular weight range 1000 to 6000. Table 2 shows that an increase in L yields a hollow fiber membrane with a smaller outside diameter (o.d.), a smaller inside diameter (i.d.), and also a decreased wall thickness; how-

TABLE 2
Effect of Length of Air Gap on Hollow Fiber Membrane Dimensions[a]

	Hollow fiber no.				
	L_1	L_2	L_3	L_4	L_5
Air gap length, cm	20	50	100	150	200
o.d., mm	1.578	1.486	1.346	1.309	1.067
i.d., mm	0.928	0.928	0.882	0.858	0.696
Fiber wall thickness, mm	0.325	0.279	0.232	0.221	0.186
o.d./i.d.	1.700	1.601	1.526	1.515	1.533

[a]Spin solution composition, wt%: polysulfone, Udel 3500, 17; PVP-10K, 17; DMAc, 66. Spinning conditions: Temperature of spin solution, 25°C; internal coagulant, water at 25°C; external coagulant: water at 17°C.

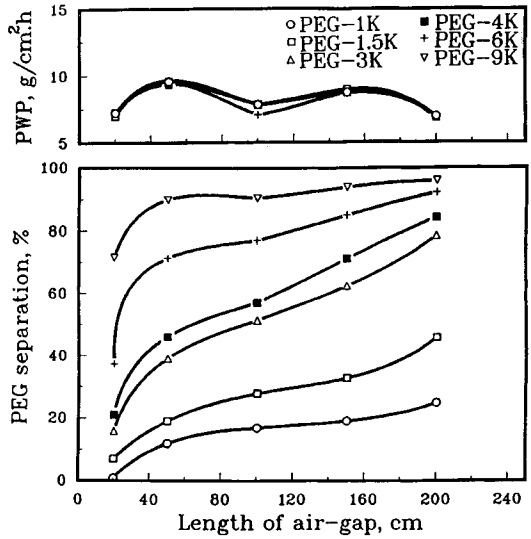

FIG. 4. Effect of length of air gap on membrane performance. Operating pressure, 20 psig; temperature, 25°C; feed rate, 0.8 m/s.

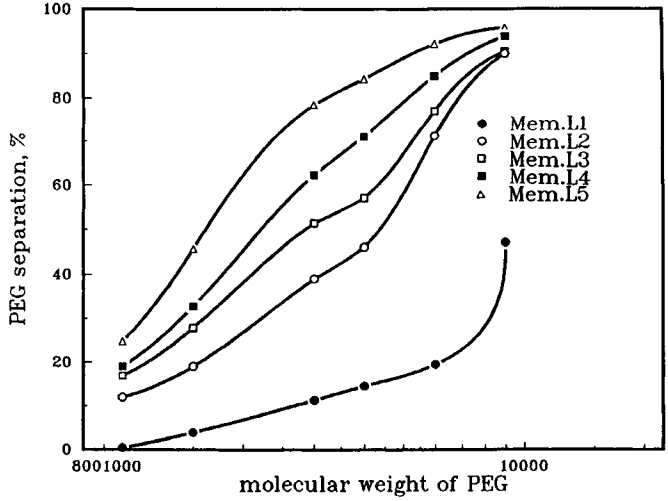

FIG. 5. Solute separation versus solute molecular weight for fibers spun at different air-gap lengths.

ever, the o.d./i.d. ratio shows an initial decrease with an increase in L from 20 to 100 cm, and then tends to remain constant for L values in the range 100 to 200 cm. Thus, in the range L = 20 to 100 cm, the rate of decrease in o.d. is more than the rate of decrease in i.d., whereas, in the range L = 100 to 200 cm, the rate of decrease in o.d. is essentially the same as the rate of decrease in i.d. Figure 4 shows that PEG separation progressively increases with an increase in L, which indicates that the average size of pores on the membrane surface in the bore decreases with an increase in L. Figure 5 (which is a replot of the separation data in Fig. 4) shows that an increase in L tends to make the above pores more uniform. The data on PWP given in Fig. 4 are particularly interesting. They show that PWP as a function of L passes through a double maximum, one at L = 50 cm and the other at L = 150 cm; further, PWP is essentially the same at L = 20 cm, L = 100 cm, and L = 200 cm. Thus L has important effects on the size, number, and distribution of pores on the membrane bore surface, and also on the resulting fiber dimensions. With an increase in L, the fiber stretches and elongates by its own weight, the polymer aggregates move closer together and rearrange themselves into a state of greater stability, resulting in a decrease in the size of aggregate pores and also a more uniform distribution of such pores on the membrane surface in the bore. The observed maxima in PWP is a reflection of the changes in pore size distribution arising from a continuous change in pore size taking place in the incipient membrane during formation. The fact that PWP at L = 20 cm is essentially the same as PWP at L = 200 cm, together with the fact that solute separations at L = 20 cm are considerably and consistently lower than those at L = 200 cm, shows that solute separation and PWP are mutually independent, which is the case in all phase inversion RO/UF membranes.

Effect of Pressure Used for Fiber Extrusion

In the spinning system used, high pressure nitrogen was utilized for fiber extrusion through the spinnerette. For a given spin solution, a higher nitrogen pressure results in a higher fiber extrusion rate. Table 3 gives data on fiber dimensions for a set of five membranes spun under different extrusion pressures [P_1 to P_5 in the range 138 to 335 kPag (20 to 50 psig)] and otherwise identical spinning conditions. Useful membranes could not be obtained under a nitrogen pressure less than 103 kPag (15 psig) for the spin solution used. The results showed that an increase in nitrogen pressure in the range 138 to 335 kPag (20 to 50 psig) increased the outer diameter of the fiber from 1.380 to 1.543 mm, and also increased the bore diameter from 0.789 to 0.936 mm, with little change in the fiber wall thickness. The UF per-

TABLE 3
Effect of Pressure Used for Fiber Extrusion[a]

	Hollow fiber no.				
	P_1	P_2	P_3	P_4	P_5
Extrusion pressure, kPag	138	172	241	310	345
psig	20	25	35	45	50
o.d., mm	1.380	1.427	1.462	1.520	1.543
i.d., mm	0.789	0.824	0.882	0.951	0.936
Wall thickness, mm	0.296	0.302	0.290	0.285	0.307
o.d./i.d.	1.749	1.732	1.658	1.598	1.648

[a]Spin solution composition, wt%: polysulfone, Udel 3500, 21; PVP (10K), 10; DMAc, 69. Temperature of spin solution, 25°C; internal coagulant, water at 25°C; external coagulant, water at 5°C; length of air gap, 82 cm.

formance of the membranes in terms of PWP and separation for PEG solutes of different molecular weights in the range 1500 to 9000 are shown in Figs. 6 and 7. Figure 6 shows that extrusion pressure has an effect on pore size distribution on the bore surface; membrane P_3 extruded at 241 kPag (35 psig) had a relatively more uniform pore size distribution. Figure 7 shows that the P_3 membrane also gave higher solute separation than the other membranes tested. Thus, the results showed the existence of an

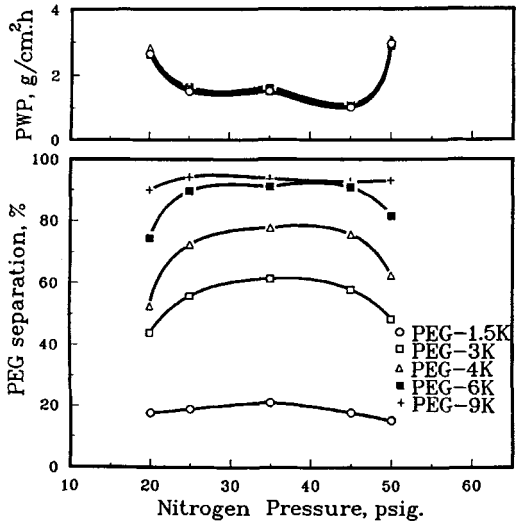

FIG. 6. Effect of nitrogen pressure on membrane performance. Operating pressure, 20 psig; temperature, 25°C; feed rate, 0.8 m/s.

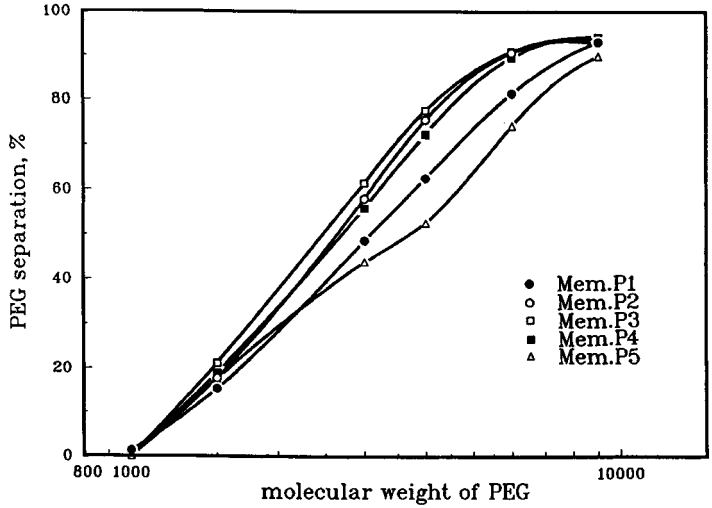

FIG. 7. Solute separation versus solute molecular weight for fibers spun under different nitrogen pressures.

optimum extrusion pressure for the spin solution resulting in the smallest average pore size and also more uniform pore size distribution on the bore surface of the membrane. The variations in the PWP data shown in Fig. 7 reflect the changes in pore size distribution arising from a continuous change in pore size taking place in the incipient membrane during formation.

CONCLUSION

The conditions used for making hollow fiber membranes have major effects on the physical dimensions and the morphology (including asymmetry of a porous structure) of the resulting membranes and hence their UF performance. This work underlines the need for further detailed cause–effect studies in the process of making hollow fiber membranes with respect to different polymer materials, spin solution compositions, and spinning conditions, so that their results on the fiber dimensions and membrane morphology, in terms of pore size, pore size distribution, and asymmetry of porous structure, can become quantitatively ascertainable and also predictable.

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