The Effects of Spinning Conditions on the Structure Formation and the Dimension of the Hollow-Fiber Membranes and Their Relationship with the Permeability in Dry–Wet Spinning Technology

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SYNOPSIS

Hollow-fiber membranes were prepared by dry–wet spinning under different spinning conditions. The used spinneret was tube-in-orfice type and the membrane material was polysulfone (Udel P-3500). *N*-methyl-2-pyrrolidinone (NMP) and water were used as solvent and coagulant, respectively. The concentration of the dope solution was 22 wt %. The effects of the three spinning factors—spinning height; extrusion rates of dope solution and inner coagulant; dimensions (inner diameter, outer diameter, and thickness) and permeation properties of the hollow-fiber membranes—were studied. The results were as follows: With changes in the spinning factors, spinning velocity and falling time before the membrane entered the water (coagulant) were changed; consequently, the structures and the dimensions of the hollow-fiber membranes varied with a certain tendency. The permeation properties of the hollow fibers were related very closely to the changes in the fibers' structures and dimensions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Ultrafiltration hollow-fiber membranes have an asymmetric structure consisting of an active skin layer and a porous support layer. The asymmetric structure of the hollow fiber is usually formed by dry–wet spinning through a phase inversion process.[1-6] Early researchers, such as I. Cabasso, studied the effect of the composition of dope solution and inner coagulant on the structure, mechanical property, and permeability of the hollow fiber; they established the foundation of the hollow-fiber formation.[7,8] In the formation of the hollow fiber by dry–wet spinning, spinning conditions affect the hollow fibers' characteristics such as structure, dimension, and permeation. As the variables in the spinning condition, we can think of chemical variables (composition of dope solution, composition of coagulant, concentration of dope solution) and rheological variables (spinning height, spinning velocity, extrusion rate of dope solution or coagulant, type of the spinneret). So far, many papers have reported studies on the effects of the composition of dope solution, composition of coagulants, and concentration of dope solution on the characteristics of the hollow fiber.[9-15]

However studies have rarely been reported on the effect of the spinning height, spinning velocity, extrusion rate of dope solution or inner coagulant, or type of the spinneret as rheological variables on the characteristics of the hollow fiber.[16-20] In the preparation of the hollow-fiber membranes for ultrafiltration, rheological variables will be very important or will be more important than the chemical variables because the dimension as well as the structure of the hollow fibers will be affected considerably by the rheological variables. The dimension of the hollow fiber is of special importance in the preparation of the module for practical use. Because the hollow-fiber membrane is self-supporting, it is also impor-

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tant that the dimension have enough mechanical strength.

In this research, the effects of the rheological variables (such as spinning height, extrusion rate of dope solution, and extrusion rate of inner coagulant) on the characteristics of the hollow-fiber membranes were studied. The purpose of this research is to establish the relationships between the rheological variables in the spinning and the characteristics of the hollow-fiber membrane. The hollow-fiber membranes were prepared by dry–wet spinning of the 22 wt % of polysulfone (Udel P-3500) in *N*-methyl-2-pyrrolidinone (NMP) at room temperature under different experimental conditions. The hollow-fiber membranes were observed with scanning electron microscopy (SEM) to study the structures and dimensions. The permeation properties were also studied.

EXPERIMENTAL

Materials

Polysulfone (Udel P-3500) was used as the membrane material because of its good chemical resistance, good mechanical strength, and good heat resistance. *N*-methyl-2-pyrrolidinone (NMP) was used as solvent. Water was used as coagulant.

Preparation of the Hollow-Fiber Membranes

Hollow-fiber membranes were prepared by dry–wet spinning of a polysulfone solution in NMP at room temperature, as shown in Figure 1. Before spinning, the polymer solution was kept for 2 days without stirring at room temperature to remove air bubbles in the solution. The composition of the polymer solution was polysulfone (PS)/NMP = 22/78 (wt/wt). Distilled water was used as inner and outer coagulant.

The polymer solution and inner coagulant, purified by the filtering impurities, were spun through a tube-in-orifice type spinneret with 0.5 mm inner diameter and 1 mm outer diameter. The extrusion rates of the polymer solution and inner coagulant were controlled by a metering pump. The hollow fibers being spun passed through the air gap and down into the water bath. The fibers were solidified in the water bath and the resulting hollow-fiber membranes were wound on the bobbin. The prepared hollow-fiber membranes were cut to a certain length, heat-treated in the 100°C water for a few hours, and dried after dipping in glycerine for the preparation of the modules.

Variables in the Spinning Condition

The variables in the spinning condition were defined and determined as follows:

Spinning height (cm) = The distance from the end of the spinneret to the water surface in the coagulation bath

Spinning velocity (cm/min) = The length of the hollow fiber spun for 10 minutes/10

Falling time (sec) = spinning height/spinning velocity

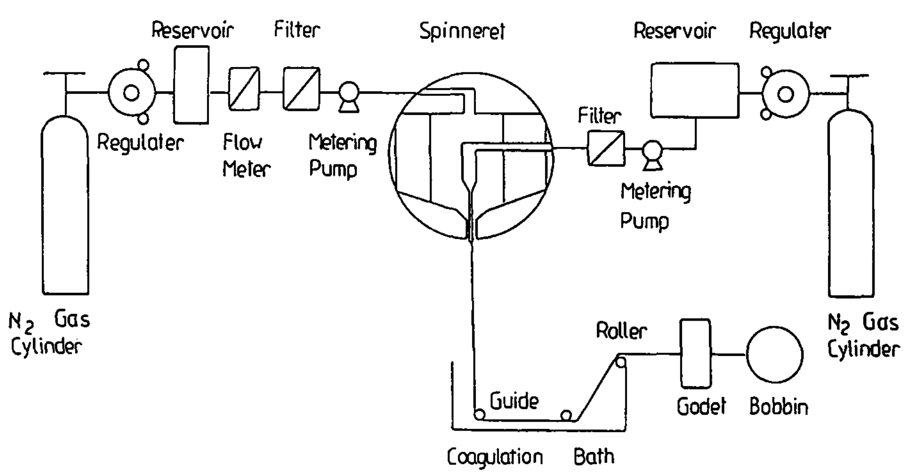


Figure 1 Schematic diagram of hollow-fiber preparation.

Extrusion rate (g/min) = Weight of the solution extruded from the spinneret for 10 minutes/10

Permeation Test

In order to determine the permeation properties of the hollow-fiber membranes, test modules were prepared by fixing six 30-cm hollow fibers to the swagelok reducing union with silicone resin followed by the curing epoxy resin. A common permeation test set was used to measure the permeability of water through the hollow fibers. The water flux was calculated from the equation below:

$$\text{Water flux (cm/min atm)} = Q/(A \times T)$$

where Q is the volume of permeate (cm^3), A is the area of the membrane (cm^2), and T is the permeation time (min).

Observation of the Membrane Structures

The structures of the hollow-fiber membrane were observed with a scanning electron microscope (JEOL Model JSM-840A). The structures of the cross section of the hollow-fiber membranes were obtained from the fracture surface after breaking the membranes in liquid nitrogen.

RESULTS AND DISCUSSION

The Effect of the Spinning Height

Figure 2 present the variations in the fiber dimension and the water flux as functions of spinning height. Here the "spinning height" means the distance between the spinneret end and the water surface in the bath. The water flux increased with increasing spinning height to 60 cm but decreased after 60 cm. This behavior was also observed by Lee et al,[20] however they had no explanation.

In order to figure out this result, the cross sections of the hollow-fiber membranes prepared at different spinning heights were carefully studied with the SEM. Figure 3 shows the SEM photographs. SEM observation of the hollow fibers showed that the structure of the hollow fibers changed with spinning heights; the hollow fiber spun from spinning height 0 cm showed two skin layers, inner and outer, and a double finger structure that developed from both inside and outside the hollow fiber. On the other hand, the hollow fiber spun from the spinning height of 60 cm showed a single inner-skin layer and a mono finger structure.

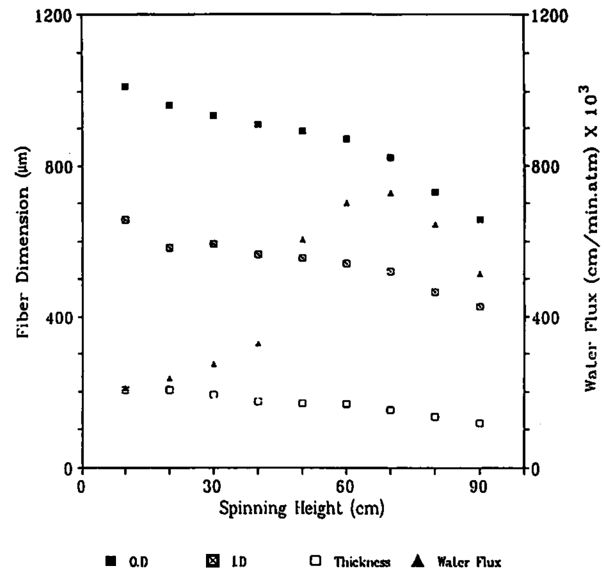


Figure 2 The effect of spinning height on the dimension and water flux of the hollow-fiber membranes. Extrusion rate of dope solution = 3 g/min. Extrusion rate of inner coagulant = 11 g/min.

The differences in the hollow fiber structures—i.e., number of skin layers and different types of finger structure—are responsible for the water flux behavior, because generally the water flux of the hollow-fiber membrane with two skin layers and a double finger structure is lower than that of a membrane with one skin layer and a mono finger structure.

The change in the hollow-fiber structures according to spinning height can be explained by the falling time, as shown in Figure 4. "Falling time" means the residence time of the hollow fiber in the air gap before entering the water during spinning. The falling time increased as spinning height increased to 60 cm but falling time decreased after that. The increase in falling time means an increase in the residence time of the hollow fiber in the air gap before entering the water during spinning. The increase in falling time with increased spinning height is a general phenomenon, but the decrease in falling time after 60 cm spinning height is not general. This decrease in falling time can be explained by the elongation of the hollow fiber from the weight of the hollow fiber which hangs from the end of the spinneret before going into the water. The weight of the hollow fiber, affecting the elongation, increases with increasing length of the hollow fiber in the air gap; this weight was almost negligible

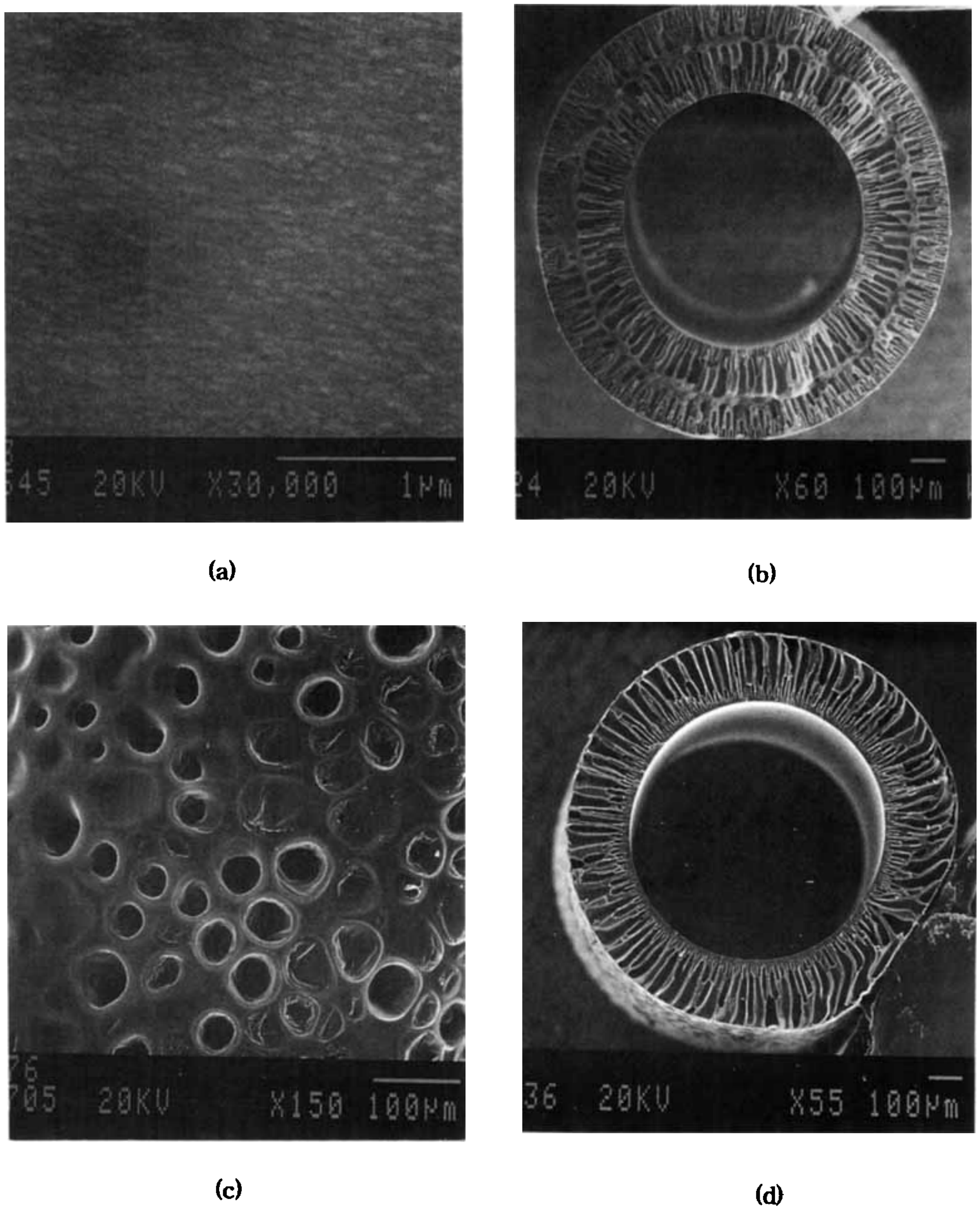
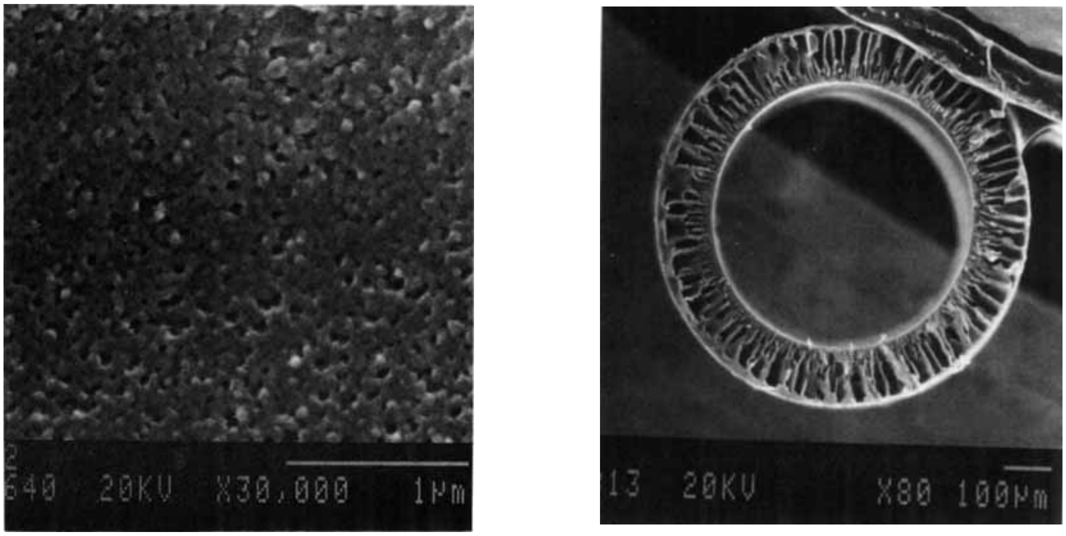


Figure 3 SEM photographs of hollow fibers spun at different spinning heights. (a) Outer surface and (b) cross section of the hollow fiber spun at 0-cm spinning height; (c) outer surface and (d) cross section of the hollow fiber spun at 60-cm spinning height; (e) outer surface and (f) cross-section of the hollow fiber spun at 80-cm spinning height.

up to 60 cm spinning height. After 60 cm spinning height, however, the weight had a greater effect and a decreased falling time resulted.

On the spinning, phase inversion occurred in both sides or on a single side, depending on the spinning conditions (Fig. 4). When the spinning height was zero (falling time was zero), the phase inversion occurred from both the inner and outer sides at the same time, so the resulting hollow fiber had two skin layers and a double finger structure. With increased falling time, phase inversion started occurring from the inner side of the hollow fiber and propagated toward the outside before the phase inversion occurred from outer side. The resulting hollow fibers showed the more porous outer skin with increased falling time. The hollow fiber spun at spinning height 60 cm (falling time 2.5 sec) showed mono-finger structure but no outer skin.



(e) (f)

Figure 3 (*Continued from the previous page*)

The hollow fiber spun at spinning height 80 cm (falling time 2.1 sec) started showing a thin and porous outer skin.

The dimensions of the hollow fibers (diameter and thickness) gradually decreased with increased spinning height, as shown in Figure 2. This result can be explained by the increase in spinning velocity. The spinning velocity as a function of spinning height is shown in Figure 4. Spinning velocity increased with increasing spinning height because of the elongation of the hollow fiber from the increasing weight of hollow fiber being spun and hung in the air gap, as mentioned above. The more elongated hollow fibers showed thinner thicknesses and smaller diameters.

The Effect of the Extrusion Rate of Dope Solution

To study the effect of the extrusion rate of dope solution on the characteristics of hollow fiber membranes, the extrusion rate of dope solution was controlled from 1.6 g/min to 4.0 g/min. Here, two spinning heights (0 cm and 65 cm) and a constant extrusion rate of inner coagulant (11 g/min) were used. The characteristics of the membrane as a function of the extrusion rate of dope solution were different at the two spinning heights.

Figure 5 presents the characteristics of the hollow-fiber membranes as a function of the extrusion rate of dope solution at 0 cm spinning height. With increasing extrusion rate of dope solution, the inner and outer diameters decreased but the thickness increased. This result can be explained by the increase in spinning velocity and the constant extrusion rate of inner coagulant, as shown in Figure 7. The spinning velocity increased with an increasing extrusion rate of dope solution but the inner coagulant extrusion rate was constant, so the ratio of spinning velocity to extrusion rate of inner coagulant was increased. As a consequence, the inner and outer diameters decreased. The thickness increased, however, due to the increase in extrusion rate of dope solution and no elongation effect in the water. The decrease in water flux with increasing extrusion rate of dope solution, shown in Figure 5, might be due to the increasing thickness of the membrane.

In the case of the hollow-fiber membrane spun at 65 cm spinning height, the effect of the extrusion rate of dope solution on the characteristics of the membrane was more complicated (Fig. 6). With increasing extrusion rate of dope solution in the range from 1.6 g/min to 2.0 g/min, the inner diameter, outer diameter, and thickness of the membrane increased, but they decreased gradually above 2.0 g/min. This result can be explained possibly by the spinning velocity shown in Figure 7. In the range from 1.6 g/min to 2.4 g/min, the spinning velocity did not increase even though the dope solution extrusion rate increased. This may be due to the die swell effect, but the exact reason is not clear. However, at a dope solution extrusion rate above 2.4 g/min, the falling time gradually decreased, partially because of the elongation effect. The elongation effect can be confirmed from the comparison of the two slopes of the spinning velocity as functions of

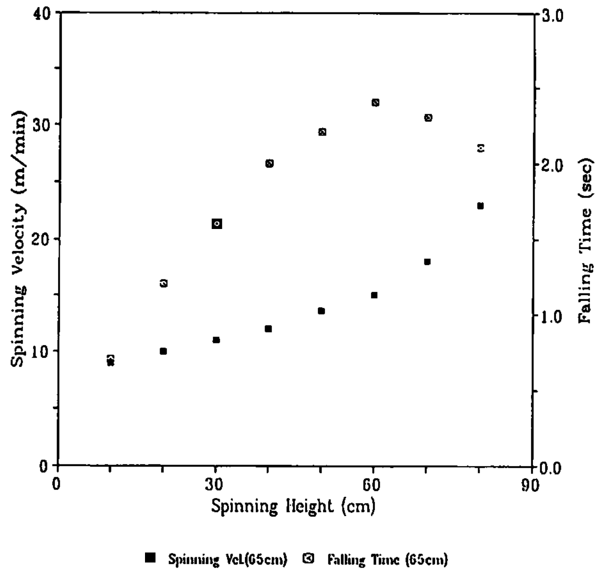


Figure 4 The effect of spinning height on the spinning velocity and falling time. Extrusion rate of dope solution = 3 g/min. Extrusion rate of inner coagulant = 11 g/min.

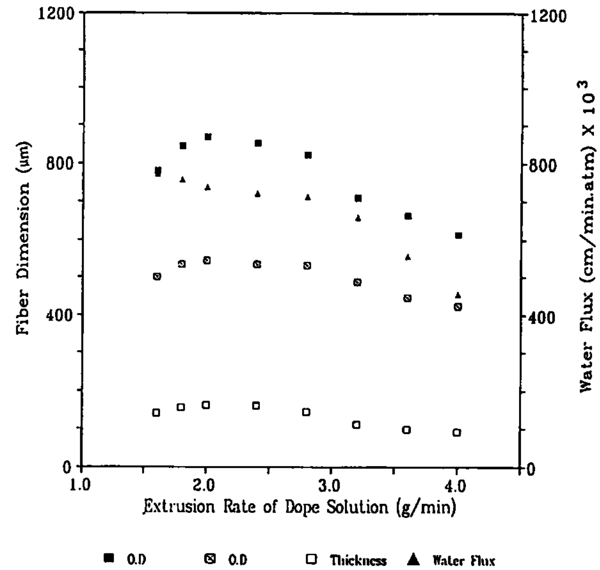


Figure 6 The effect of the extrusion rate of dope solution on the dimension and water flux of the hollow fibers spun at 65-cm spinning height. Extrusion rate of inner coagulant = 11 g/min.

the extrusion rate of dope solution obtained from 0 cm and 65 cm spinning heights (Fig. 7). The slope of the spinning velocity as a function of the extrusion rate of dope solution at 65 cm spinning height was higher than that at 0 cm spinning height. Because of this kind of spinning velocity behavior, the dimension of the membrane varied as shown in Figure 6.

The water flux of the hollow-fiber membrane spun at 65 cm decreased with the increased extrusion rate of dope solution (Fig. 6). This result was mainly due to the change in the membrane structure with the falling time, explained as part of the effect of the spinning height.

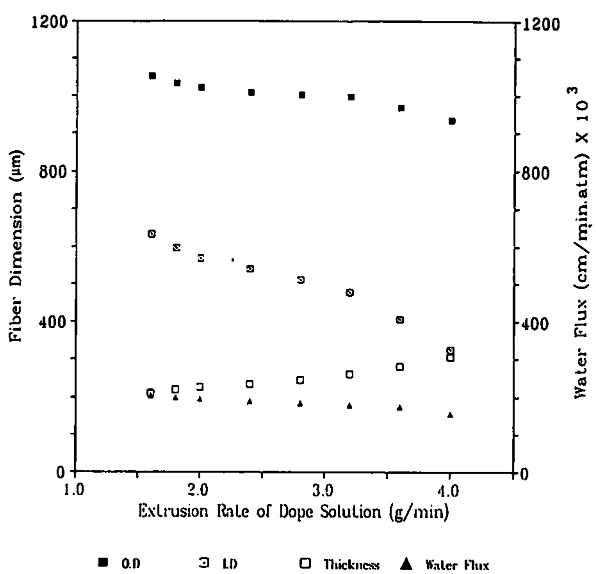


Figure 5 The effect of the extrusion rate of dope solution on the dimension and water flux of the hollow fibers spun at 0-cm spinning height. Extrusion rate of inner coagulant = 11 g/min.

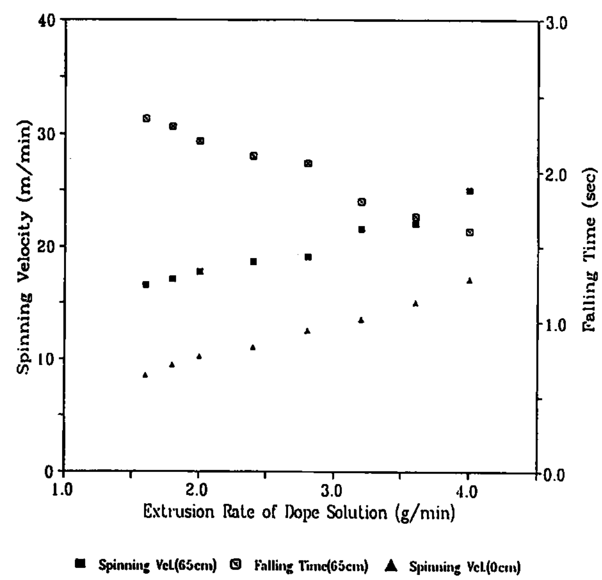


Figure 7 The effect of the extrusion rate of dope solution on spinning velocity and falling time at spinning heights of 0 cm and 65 cm. Extrusion rate of inner coagulant = 11 g/min.

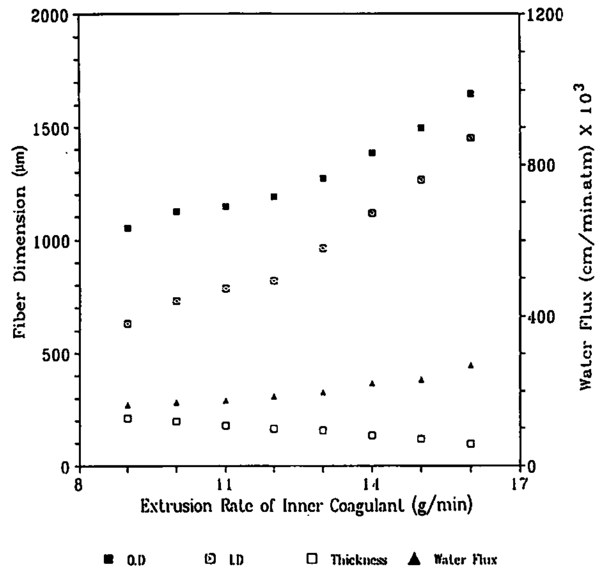


Figure 8 The effect of extrusion rate of inner coagulant on the dimension and water flux of the hollow fibers spun at 0-cm spinning height. Extrusion rate of dope solution = 3 g/min.

The Effect of the Extrusion Rate of the Inner Coagulant

In order to study the characteristics of the hollow-fiber membranes according to the variation in the extrusion rate of the inner coagulant, the inner coagulant extrusion rate was varied from 9 g/min to 16 g/min. Here also, the two spinning heights of 0 cm and 65 cm were used.

Figure 8 shows the characteristics of the membranes spun at spinning height 0 cm as functions of the inner coagulant extrusion rate. With increased inner coagulant extrusion rate, both inner and outer diameters increased; the inner diameter, however, increased more. Consequently, the thickness decreased. With the decreasing thickness, the water flux increased. The reason for this result was the expansion of the hollow fiber due to the increased pressure inside, which resulted from the increase in the inner coagulant extrusion rate. The spinning velocity, shown in Figure 10, also increased.

In the case of the spinning at 65 cm, the dimension and water flux of the membrane were more complicated, as in the case of the effect of the dope solution extrusion rate. Figure 9 presents the characteristics of the hollow-fiber membrane according to the extrusion rate of the inner coagulant.

With the inner coagulant extrusion rate increasing to 12 g/min, the membranes' inner and outer diameters increased; after that point, however, they decreased. The thickness also gradually decreased. This change in membrane dimension with inner coagulant extrusion rate could be explained by the combination of the expansion and elongation of the hollow fibers. In other words, until the extrusion rate of the inner coagulant reached 12 g/min the expansion effect was dominant, but after that point the elongation effect was dominant. Therefore, when the expansion effect was dominant the diameters increased and when the elongation effect was dominant, the diameters decreased.

The water flux increased as the inner coagulant extrusion rate started to increase, but it decreased after 12 g/min. This result was due to the change of the membrane structure as explained in the effect of spinning height on the water flux. The membrane structure varied with change in the extrusion rate of the inner coagulant as follows: a finger structure with double skin layers (9 g/min), a finger structure with a single skin layer (12 g/min), and a finger structure with double skin layers (16 g/min). The change in the membrane structure was related to the falling time, shown in Figure 10, and the extrusion rate of the inner coagulant. The water flux also changed according to the variation of the hollow-fiber membrane structure.

CONCLUSION

The study of the relationship between the characteristics of the hollow-fiber membranes and rheo-

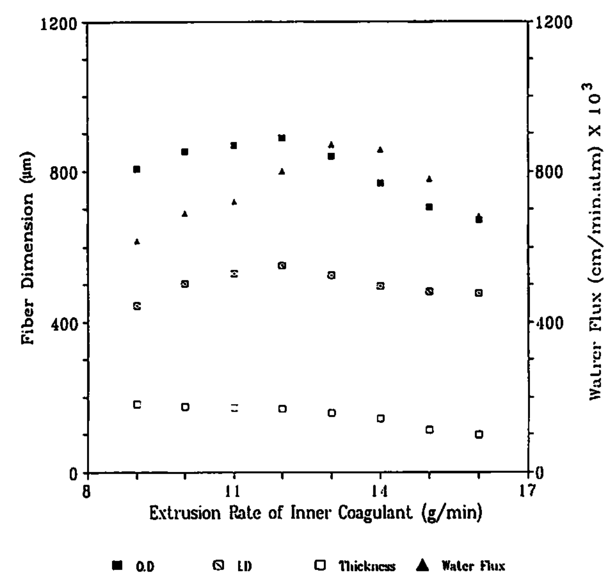


Figure 9 The effect of the extrusion rate of inner coagulant on the dimension and water flux of the hollow fibers spun at 65-cm spinning height. Extrusion rate of dope solution = 3 g/min.

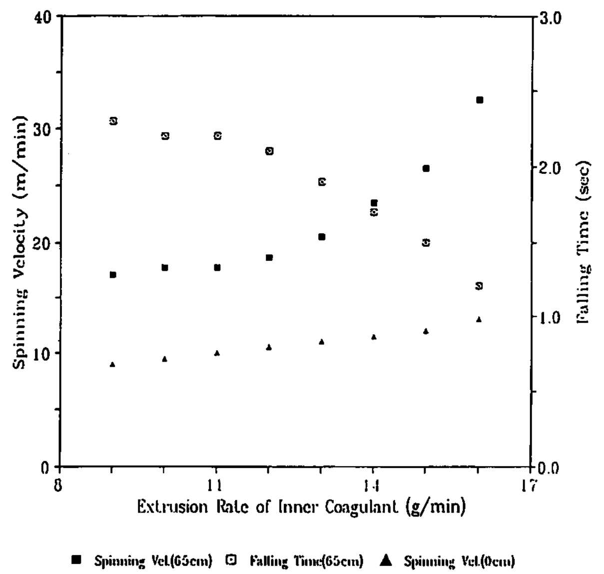


Figure 10 The effect of the extrusion rate of inner coagulant on spinning velocity and falling time at spinning heights of 0 cm and 65 cm. Extrusion rate of dope solution = 3 g/min.

logical variables of the spinning condition provided very useful information for the preparation of the hollow-fiber membranes by dry–wet spinning. The rheological variables were very closely related to the membrane structure, dimensions, and permeability.

The variation in the spinning height affected the time when the being-spun hollow fiber was entering the water (outer coagulant) and eventually changed the structure of the hollow fiber. In addition, the height induced the elongation of the hollow fiber during the spinning and resulted in variation of the dimensions of the hollow fiber.

The extrusion rates of the dope solution and the inner coagulant influenced the structure formation of the hollow fiber being spun at 65 cm spinning height, but had no influence at 0 cm spinning height. The dimension of the hollow fiber was seriously affected by those two factors.

The variation in the structure and/or dimensions of the hollow fiber affected the water permeability. The water permeability always appeared to be the result of the combination of structure effect and dimension effect.

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