Spinning of Cellulose Acetate Hollow Fiber by Dry–Wet Technique of 3C-Shaped Spinneret

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SYNOPSIS

Cellulose acetate hollow fibers were spun by a new method—a dry–wet spinning technique of a 3C-shaped spinneret. The spinning technique parameters effecting the form and the reverse osmosis performances of the hollow fiber were investigated in detail, such as polymer concentration, the kind of solvent and additive, spinneret temperature, extrusion rate, evaporation distance, and take-up rate. Heat treating for different times in several treating baths was tested. The results showed that cellulose acetate hollow fiber spun by this method is feasible and is a kind of "loose" reverse osmosis membrane and suitable to operate at ultralow pressure, 0.8 MPa, and exhibits a higher flux rate at a salt rejection of 60–85% for tap water. Cellulose acetate hollow fiber for ultralow pressure reverse osmosis should find wide application in industrial processes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Since Monsanto developed an asymmetric cellulose acetate (CA) hollow fiber in the late 1960s, CA hollow fiber membranes have been applied in the purification of brackish water and municipal sewage waste water and have established a steady market.[1,2] Although other kinds of membrane materials for hollow fiber have been extensively investigated, because of its wide source, low cost, easy formation, and good reverse osmosis (RO) performances, etc., CA still remains one of the most important membrane materials for RO.[3]

At present, there are three spinning methods to prepare CA hollow fiber:

1. Melt spinning, in which CA with a plasticized mixture containing dimethyl phthalate and glucerol is spun.[4]
2. Dry spinning, in which CA predissolved in a volatile solvent mixture (methyl formate and propylene oxide) is spun into an evaporative column.[5]
3. Dry–jet wet spinning, in which a CA solution in acetone–formamide is spun and coagulated in a water bath at 0°C.[6]

In the above methods, the spinnerets used are all tube-in-orifice jets. However, the spinnerets in a production-line assembly need multiple groups of orifices because of the low productivity of one orifice, especially in the dry–jet wet spinning method. The multiorifice spinnerets of a tube-in-orifice jet require a high degree of precision in design and can most easily cause eccentricity. The other problems encountered are the delivery of identical quantities of dope to each orifice and the instantaneous self-adjustment of the spinneret's internal pressure if an orifice is plugged during spinning.[7] To solve these problems, we used another kind of spinneret—a 3C-shaped orifice—to spin CA hollow fibers. Although 3C-shaped orifices have been used to spin polysulfone hollow fiber for ultrafiltration,[8] CA hollow fiber spun by this method has been hardly reported until now. In this article, we report the results of our studies on the spinning of CA hollow fiber and elaborate on the variable parameters involved in the spinning process.

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Journal of Applied Polymer Science, Vol. 62, 129–133 (1996)

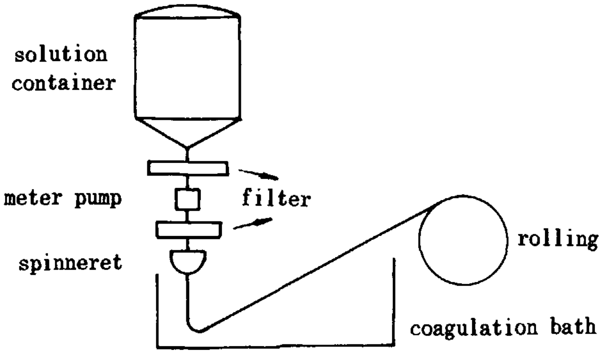

Figure 1 Schematic of hollow fiber spinning.

EXPERIMENTAL

Spinning

A 3C-shaped orifice, dry–wet spinning technique was employed. This process utilized a very short air quench exposure with ultimate gelation of the polymer thread in a subsequent bath. Many parameters were involved in the dry–jet wet technique, and these interact during the extrusion/coagulation steps. The principal variables include dope composition, dope viscosity, spinneret temperature, extrusion rate, spinneret distance from the coagulation bath, coagulation temperature, and fiber draw rate (take-up rate). In this study, CA hollow fibers with diverse properties were spun by varing spinning conditions. The main steps of the process shown in Figure 1 are described here:

1. A viscous solution of CA in solvents such as acetone or dioxane was prepared.
2. The spinning solution was prefiltered and then filtered again while being pumped to the spinning jet.
3. The solution extruded through the jet was drawn into a coagulation bath.
4. The nascent fiber solified in the coagulation bath. The fiber was directly transferred from the bottom of the coagulation bath onto a self-advancing godet, then rolled up.

Spinneret

A segmented-arc spinneret with three or six holes was used to spin CA hollow fiber. The schemes of its segmented-arc cross section and six-hole arrangment are shown in Figures 2 and 3. The solution extruded through the 3C-shaped orifice rapidly coalesces to complete the annular configuration. There is no need for gas injection to prevent collapse of the hollow fiber, because the gas is drawn through the unwelded gaps. Although this type of spinneret also requires a high degree of precision in design and machining, the spun hollow fiber was not eccentric as it was by the tube-in-orifice. In addition, its multiorifice spinnerets are easy to machine.

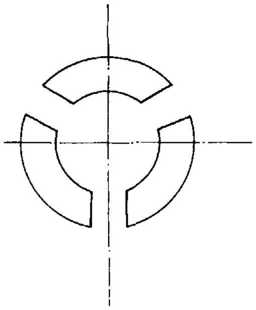

Figure 2 3C-shaped orifice face.

Measurement of RO Performance

The flux rates were determined at the operation pressure of 0.8 MPa on home-made equipment.[9] The salt concentrations were determined by an electroconductivity monitor. The tap water was used as the feed.

RESULTS AND DISCUSSION

Effect of the Spinning Solution

The viscosity of the spinning solution is a key parameter to form a hollow fiber by the 3C-shaped spinneret and is far more important than by the tube-in-orifice spinneret. If the viscosity of the spinning solution is lower, the dope through the spinneret tends to flow in a natural state so that the inside bore of the nascent fiber will be too small or difficult to form. If the viscosity of the spinning so-

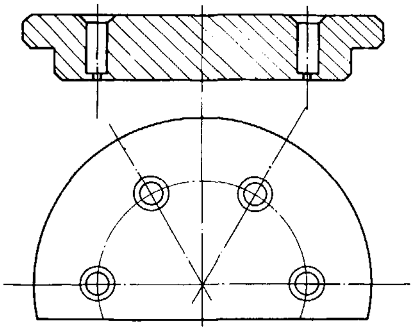

Figure 3 Six-hole layout of 3C-shaped spinneret.

Table I Effect of CA Concentration

	Polymer Concentration (%)						
	28.0	27.0	26.5	26.0	25.7	25.5	25.0
Salt concentration (%)	83.5	78.3	71.6	64.7	40.0	35.0	16.0
Flux rate (GFD)	4.1	4.9	3.0	6.4	5.1	4.0	4.6

lution is higher, not only deaeration of the spinning solution will be difficult, but also the dope delivered through the spinneret will emerge as a twisting deformation, even breaking off. Therefore, the viscosity range is generally 100–500 poise. If the composition is changed, such as the content of CA or the type or content of solvents and additives, its viscosity must be controlled strictly in the forming range of the hollow fiber. The hollow fiber for RO performances of different concentrations shown in Table I cannot be compared absolutely, especially when the concentration is 25–28%. The spinning viscosity can be achieved only by the adjustment of the additive content and the type of solvent. The type of solvent affects not only the CA solubility, but also the coagulating rate and the formation of the hollow fiber (Table II). The hydrophilic solvent will accelerate the coagulating rate of the nascent fiber and easily set the fiber cross section. But we must consider the solvents that have good volatility so that the external skin of the hollow fiber occurs as a thin compact layer before the nascent fibers enter into the coagulating bath because of the solvent's volatilizing. The thin compact layer controls the hollow-fiber performances for RO. The results show that the appropriate concentration of CA is 25–28%. The solvents are acetone, dioxane, or their mixture; the additives are formide, meilic acid, or other inorganics and organics.

Effect of Spinneret Temperature

Spinneret temperature controlled directly the viscosity of the dope at the 3C-shaped hole and the drawing of the nascent fibers. The determination of the temperature range at first should meet the demand of the dope viscosity to ensure the forming of the hollow fiber. On the basis of the temperature range, the spinneret temperature can be determined according to the boiling point of the solvent and the additive to obtain an appropriate evaporating speed of the nascent fiber. Generally, the spinneret temperature should be controlled at about 10–20°C below the boiling point of the composition.

Effect of Extrusion Rate

The extrusion rate is another key parameter to the forming of the hollow fiber in the dry–wet spinning technique of the 3C-shaped spinneret because the 3C-shaped spinneret is designed in light of the viscous elasticity of the spinning fluid at a certain extrusion rate.[8] The spinning fluid shear-flowing into the hole canal exists as a normal stress difference. When it is extruded out through the 3C-shaped spinneret, the nascent fiber will emerge as "the jet swelling effect," the famous "Barus effect." Further, the extrudate rapidly coalesces to complete the annular configuration. The difference of the extrusion rate will change the stress situation and the viscous elasticity of the dope. When the extrusion rate is too slow, the extrudate will free-flow rapidly along the spinneret surface so as to make the spinning flow unstable and difficult to form the fiber. With increase of the extrusion rate, the spinning flow will convert from a "free-flow" type into a "swelling" type and emerge as the cross-section change shown

Table II Effect of the Solution Composition

	Solvent Composition					
	Dioxane Formide	Dioxane Acetone Formide	Acetone Formide	Acetone Formide MA	Acetone Formide Alcohol	Acetone Formide DMF
Salt rejection (%)	67.3	83.5	78.3	70.0	60.0	63.0
Flux rate (GFD)	3.4	4.1	4.9	5.1	4.3	4.5

MA, meilic acid; DMF, dimethylformamide.

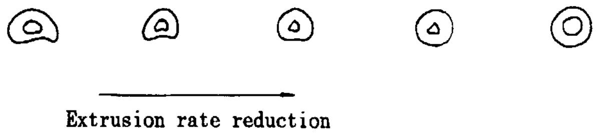

Figure 4 Effect of extrusion rate on the forming of hollow fiber.

in Figure 4. When the extrusion rate is high enough to form the hollow fiber, further increase of the extrusion rate is possible. But the increased range of the CA solution depends on the viscous plastics of the solution. The extrusion rate cannot become too high; otherwise, the spinning fluid will be converted into "cracking" type, which is also an unstable flow.

Effect of Evaporating Distance

In the dry–wet technique of the tube-in-orifice, the evaporating distance combined with the take-up rate mainly controlled the evaporating rate of the solvent in the spinning fluid to obtain satisfactory RO performances. But in the dry–wet technique of the 3C-shaped spinneret, the evaporating distance was used mainly to control the forming of the hollow fiber and the cross-section diameter (external/internal diameter). It did not play a main role in providing the hollow-fiber performances for RO as did the other technique parameters. Generally, we controlled the evaporating distance between 2 and 6 cm. The external diameter was 200 μm.

Effect of Take-up Rate

The take-up rate is a parameter cooperating tightly with the extrusion rate and depends on the drawing of the spinning fluid. The spinning fluid through the 3C-shaped spinneret can draw the gas from the unwelded gaps at an appropriate take-up rate, so that the spinning fluid will have to be self-supporting to form the hollow fiber. The cross-section change of the fiber at the different take-up rates is shown in Figure 5. On the basis of the hollow fiber forming, further increase of the take-up rate will make the wall of the hollow fiber thinner so as to increase the flux rate of the hollow fiber. But when increase of the take-up rate is high enough for the polymer molecular orientation of the hollow fiber to occur, its salt rejection will increase or its flux rate will decrease. Generally, the take-up rate will be controlled in this range.

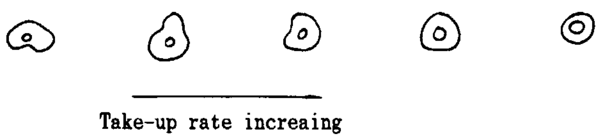

Figure 5 Effect of take-up rate on the forming of the hollow fiber.

Effect of Heat Treating

CA hollow fibers spun by the 3C-shaped spinneret were treated in several treating baths at 80°C for different times. The results in Tables III and IV show that the salt rejection of the hollow fiber will increase but that the flux rate decreases, apparently with increase of the heat-treating time.

The effect of the heat-treating time on RO performances of the hollow fiber spun by the 3C-shaped spinneret has the same change rule as that by the tube-in-orifice.[10] But the improvement of the CA hollow fiber RO performances in the several heat-treating baths is not as apparent as by the tube-in-orifice.

CONCLUSION

The spinning of CA hollow fiber by the 3C-shaped spinneret, dry–wet spinning technique is feasible. The 3C-shaped spinneret compared with the traditional tube-in-orifice has some advantages: realization of a multiorifice and no eccentricity of the hollow fiber. The key to the forming of the hollow fiber is the appropriate viscosity of the spinning solution, the extrusion rate, the evaporating distance, and take-up rate. This technique is advanced.

CA hollow fiber spun by this method is a kind of "loose" RO membrane and is suitable to operate at an ultralow pressure of 0.8 MPa and a high flux rate at the salt rejection of 60–85%. It should find wide application in industrial processes.

Table III Effect of Heat-Treating Time

	Heat-treating Time (min)				
	20	15	10	5	0
Salt rejection (%)	81.25	74.5	79.6	62.1	60.3
Flux rate (GFD)	0.47	0.47	0.39	0.87	0.93

Heat-treating temperature: 80°C; heat-treating medium: water.

Table IV Effect of Heat-Treating Medium

Medium	Non-treating	Distilling Water	0.4% SDBS	0.4% SLS	0.4% Triacetin	0.4% OP10
Rejection (%)	64.7	75.0	65.0	74.7	71.9	71.9
Flux rate (GFD)	6.4	2.7	1.2	0.8	1.19	2.1

Heat-treating temperature: 80°C; heat-treating time: 10 min. SDBS, sodium dodecyl benzene sulfonate; SLS, sodium lauryl sulfate.

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Received January 16, 1996
Accepted April 11, 1996