## Fundamental Understanding of the Effect of Air-Gap Distance on the Fabrication of Hollow Fiber Membranes

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ABSTRACT: The objectives of this work are, fundamentally, to understand hollow fiber membrane formation from an engineering aspect, to develop the governing equations to describe the velocity profile of nascent hollow fiber during formation in the air gap region, and to predict fiber dimension as a function of air-gap distance. We have derived the basic equations to relate the velocity profile of a nascent hollow fiber in the air-gap region as a function of gravity, mass transfer, surface tension, drag forces, spinning stress, and rheological parameters of spinning solutions. Two simplified equations were also derived to predict the inner and outer diameters of hollow fibers. To prove our hypotheses, hollow fiber membranes were spun from 20: 80 polybezimidazole/polyetherimide dopes with 25.6 wt % solid in N.N-dimethylacetamide using water as the external and internal coagulants. We found that inner and outer diameters of as-spun fibers are in agreement with our prediction. The effects of air-gap distance or spin-line stress on nascent fiber morphology, gas performance, and mechanical and thermal properties can be qualitatively explained by our mathematical equations. In short, the spin-line stresses have positive or negative effects on membrane formation and separation performance. A high elongational stress may pull molecular chains or phaseseparated domains apart in the early stage of phase separation and create porosity, whereas a medium stress may induce molecular orientation and reduce membrane porosity or free volume. Scanning electron microscopic photographs, coefficient of thermal expansion, and gas selectivity data confirm these conclusions.  $T_{\sigma}$  of dry-jet wet-spun fibers is lower than that of wet-spun fibers, and  $T_g$  decreases with an increase in air-gap distance possibly because of the reduction in free volume induced by gravity and elongational stress. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 379-395, 1999

**Key words:** hollow fiber membrane; membrane formation; blend membrane; air-gap distance effect; phase inversion

### **INTRODUCTION**

Polymeric hollow fiber membranes are marketdriving, high-performance products. In many cases, polymeric hollow fiber membranes were produced prior to the fundamental understanding of detailed fabrication mechanisms. Even today, most membrane scientists admit that they understand hollow fiber formation mechanisms qualitatively, but not quantitatively. New hollow fiber membranes were prepared or invented mainly based on their experience, empirical data, limited qualitative and scientific understanding, and luck. Therefore, research on polymeric mem-

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branes has emerged as one of the fastest growing research areas these days.

In fact, modern asymmetric membrane fabrication technologies are extensions of the Loeb-Sourirajan technique,<sup>1</sup> developed for reverse osmosis applications 40 years ago. Basically, they used the phase-inversion technique to fabricate integrally skinned asymmetric membranes. In this method, there are three steps involved in fiber formation: dope preparation, casting/spinning, and coagulation (or phase inversion). Many authors<sup>2-4</sup> have reviewed the principles of asymmetric membrane formation. However, most attention has been given to wet and thermal phaseinversion processes for the preparation of asymmetric flat membranes. Several scientists have attempted to qualitatively or quantitatively simulate the phase-inversion process and solvent exchange mechanisms during the flat membrane formation using various thermodynamic and diffusion kinetic theories.<sup>5–9</sup>

Although their works are important and interesting, their theories might need further modifications to be applied to hollow fiber membrane fabrication. It is due to the fact that it is difficult to simulate the hollow-fiber spinning process by adopting the process conditions developed for asymmetric flat membranes. The controlling factors for hollow fiber morphology are quite different from those for flat membranes. For example, there are two coagulations taking place in hollow fiber spinning (internal and external surfaces), whereas there is only one major coagulation surface for an asymmetric flat sheet membrane. If liquids are used as bore fluids, the internal coagulation process for a hollow fiber starts immediately after extrusion from a spinneret and then the fiber goes through the external coagulation, whereas there is usually a delay period for an asymmetric flat membrane before immersing it into a coagulant. In addition, the spinning dope suitable for fabricating hollow fibers generally has a much greater viscosity and elasticity than that for flat membranes. Furthermore, the hollow fiber formation is usually taken place under tension or stress.

Recently, Chung and coworkers<sup>10–13</sup> have found that air-gap distance and elongational stress play important roles on the mass-transfer fluxes and spinodal decomposition in Markoffian and Onsager's thermodynamic systems, as well as hollow fiber formation. Previous works also suggested that the main parameters affecting hollow fiber formation are rheological properties of spin-



**Figure 1** Schematic diagram of the hollow fiber spinning apparatus. HPLC (high-pressure liquid chromatography).

ning solution, bore fluid and external coagulant's chemistry and flow rates, dope flow rate, shear stress within an annular orifice of the spinneret, spinneret design parameters, and temperature.<sup>14–17</sup> These works motivate us further to understand the governing equations for the hollow fiber membrane formation.

To our knowledge, very rare attention has been given to describe mathematically the hollow fiber membrane formation. Previous works were mainly on the analyses of wet spinning fibers, <sup>18,19</sup> melt spinning fibers, and hollow fibers.<sup>20–23</sup> In this article, we intend to extend our approaches to derive the basic equations for hollow fiber membrane formation. To elucidate our analysis, we use polybenzimidazole (PBI) and polyetherimide (PEI) blend fibers as an example to amplify the effect of elongational stress or air-gap distance on hollow fiber membrane formation. PBI and PEI form miscibility blends in the forms of powders, flat dense film, solid fiber, and hollow fiber membranes.<sup>25–28</sup>

## UNDERSTANDING OF NASCENT HOLLOW FIBER FORMATION

Figure 1 illustrates a dry-jet wet-spinning process for the fabrication of hollow fiber membranes. Because this process is complicated, we focus our study on the air-gap region and make the following assumptions to simplify the analysis in Figure 2:

1. End effects are neglected.



**Figure 2** Schematic diagram and stress tensors of nascent hollow fibers in the air-gap region. (a) Schematic of dry-jet wet spinning of a hollow fiber by immersion precipitation after an air-gap. (b) Coordinates and stress tensors on the external surface.  $\xi_i$  is the coordinate moving with the film.

- 2. The exchange rates of nonsolvents (coagulants) and solvents are equal.
- 3. Density difference between nonsolvents (coagulants) and solvents is negligible.
- 4. Density of nascent hollow fiber remains constant during the formation.
- 5. Convective flow and convective mass transfer within the system are neglected.
- 6. The flow is isothermal and axisymmetric steady.
- 7. The die swell near the spinneret is neglected.

These assumptions might be applicable in the early stage of membrane formation if the precipitation process and the spinning speed are relatively slow. Then the differential equations of continuity, motion, and mass transfer for the nascent hollow fiber in cylindrical coordinates  $(r, \theta, z)$ 

may be described as follows  $^{18-23,29}$ :

Equation of continuity:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(\rho_{h}r\nu_{h,r}\right) + \frac{\partial}{\partial z}\left(\rho_{h}\nu_{h,z}\right) = 0 \tag{1}$$

Equation of momentum:

$$\rho_{h}\left(\nu_{h,r}\frac{\partial\nu_{h,r}}{\partial r}+\nu_{h,z}\frac{\partial\nu_{h,r}}{\partial z}\right) = -\frac{\partial p}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\tau_{rr}\right) + \frac{\partial\tau_{rz}}{\partial z}$$
(2)

$$\rho_{h}\left(\nu_{h,r}\frac{\partial\nu_{h,z}}{\partial r}+\nu_{h,z}\frac{\partial\nu_{h,z}}{\partial z}\right) = -\frac{\partial p}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\tau_{rz}\right) + \frac{\partial\tau_{zz}}{\partial z} + \rho_{h}g \quad (3)$$

Equation of mass transfer (solvent) in a nascent hollow fiber:

$$\nu_{h,r} \frac{\partial C_h^s}{\partial r} + \nu_{h,z} \frac{\partial C_h^s}{\partial z} = \left(\frac{1}{r} \frac{\partial}{\partial r} \left( D_{sp} r \frac{\partial C_h^s}{\partial r} \right) + \frac{\partial}{\partial z} \left( D_{sp} \frac{\partial C_h^s}{\partial z} \right) \right) \quad (4)$$

In eqs. (1)–(4),  $\rho_h$  is the density of nascent hollow fibre,  $\nu_{h,r}$  and  $\nu_{h,z}$  are the velocities of r- and z-components of nascent hollow fiber, respectively.  $C_h^s$  is the solvent concentration in a nascent hollow fiber,  $D_{sp}$  is the diffusion coefficient of solvent in a nascent hollow fibre, g denotes the gravitational constant, p is the isotropic pressure, and  $\tau_{ij}$  is the extra stress. Herein, we make further assumptions (Fig. 2): (1)  $\nu_h$  depends on z only and is independent of r, and (2)  $D_{sp}$  is constant. Then, eqs. (1)–(4) become as follows with the aid of the previous assumptions 2 and 3 ( $\rho_h$  is independent of z and constant):

$$\frac{\partial}{\partial z} \left( \rho_h \nu_{h,z} \right) = 0 \tag{5}$$

$$\rho_h \nu_{h,z} \frac{\partial \nu_{h,z}}{\partial z} = -\frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \tau_{rz} \right) + \frac{\partial \tau_{zz}}{\partial z} + \rho_h g \quad (6)$$

$$\nu_{h,z} \frac{\partial C_h^s}{\partial z} = D_{sp} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \; \frac{\partial C_h^s}{\partial r} \right) + \frac{\partial^2 C_h^s}{\partial z^2} \right)$$
(7)

The boundary conditions are as follows:

(i) at 
$$z = 0$$
,  $v_{h,z} = v_{h,0}$ ;  $C_h^s = C_{h,0}^s$  (8)

(ii) at 
$$z = L$$
,  $v_{h,z} = v_{h,L}$ ;  $C_h^s = C_{h,L}^s$  (9)  
(iii) at  $z = R$   $v_{h,z} = v_{h,L}$  (10)

(111) at 
$$r = R_i, \ \nu_{h,z} = \nu_{b,z}$$
 (10)

(iv) at 
$$r = R_o$$
,  $D_{sp} \frac{\partial C_h}{\partial r} = 0$  (11)

(v) at 
$$r = R_i$$
,  $D_{sp} \frac{\partial C_h^s}{\partial r} = k_i (\overline{C_h^s} - \overline{C_b^s})$  (12)

In eq. (12),  $k_i$  is mass transfer coefficient of solvent at the inner interface and is assumed to be constant.  $\overline{C}_h^s$  and  $\overline{C}_b^s$  represent the average solvent concentrations in nascent hollow fiber and bore fluid, respectively. In an ideal case of a dryjet wet-spinning process, eq. (11) implies that there is no solvent evaporation and no humidityinduced phase separation process on the external skin of a nascent hollow fiber. This equation may be valid if a high boiling solvent was used for the dope preparation and if the spinning was conducted at a low temperature with a short air-gap distance. Of course, this equation can easily be modified to incorporate the effect of solvent evaporation if the right-hand term of eq. (11) becomes nonzero. Multiplying both sides of eqs. (5)–(7) by  $2\pi r dr$ , one can integrate and then average these equations over the cross section from  $r = R_i$  to  $R_o$ at each value of z to yield the following equations:

$$Q_{hw} = \pi (R_o^2 - R_i^2) \rho_h \bar{\nu}_{h,z} = \text{constant} \qquad (13)$$

$$\pi (R_o^2 - R_i^2) \rho_h \bar{\nu}_{h,z} \frac{\partial \bar{\nu}_{h,z}}{\partial z} = \pi (R_o^2 - R_i^2) \rho_h g$$
$$- \pi (R_o^2 - R_i^2) \frac{\partial p}{\partial z} + 2 \pi [r(\tau_{rz}$$
$$- r' \tau_{zz})]_{r=R_i}^{r=R_o} + \frac{\partial}{\partial z} \int_{R_i}^{R_o} 2 \pi \tau_{zz} r \ dr \quad (14)$$

$$\bar{\nu}_{h,z} \frac{\partial \overline{C_h^s}}{\partial z} = -\frac{2R_i k_i}{R_o^2 - R_i^2} \left( \overline{C_h^s} - \overline{C_b^s} \right) + D_{sp} \frac{\partial^2 \overline{C_h^s}}{\partial z^2} \quad (15)$$

The last two terms of eq. (14) were obtained using the Leibnite formula for differentiating an integral as follows (29):

$$\frac{d}{dt} \int_{a(t)}^{b(t)} f(x, t) dx = \int_{a(t)}^{b(t)} \frac{\partial f}{\partial t} dx + \left( f(b, t) \frac{db}{dt} - f(a, t) \frac{da}{dt} \right)$$
(16)

Thus,

$$\begin{aligned} \frac{\partial}{\partial z} \int_{R_i}^{R_o} 2\pi\tau_{zz} r \ dr &= \int_{R_i}^{R_o} 2\pi r \ \frac{\partial\tau_{zz}}{\partial z} \ dr \\ &+ 2\pi\tau_{zz}|_{r=R_o} R_o \ \frac{\partial R_o}{\partial z} - 2\pi\tau_{zz}|_{r=R_i} R_i \ \frac{\partial R_i}{\partial z} \\ &= \int_{R_i}^{R_o} 2\pi r \ \frac{\partial\tau_{zz}}{\partial z} \ dr + 2\pi [rr'\tau_{zz}]_{r=R_i}^{r=R_o} \quad (17) \end{aligned}$$

where,

$$r' = \frac{\partial R}{\partial z} \tag{18}$$

and

$$\int_{R_i}^{R_o} 2\pi r \frac{\partial \tau_{zz}}{\partial z} dr = \frac{\partial}{\partial z} \int_{R_i}^{R_o} 2\pi \tau_{zz} r dr - 2\pi [rr' \tau_{zz}]_{r=R_i}^{r=R_o} \quad (19)$$

Equations (13)–(15) are the basic governing equations describing the relationship among dope flow rate, process conditions, spinning line stress, solvent mass transfer rate, solvent concentration, and various parameters during dry-jet wet-spun nascent hollow fiber formation. These equations are no longer valid and need severe modifications if those assumptions used in the derivation were not held.

The stress at boundary condition is more complicated.<sup>30,31</sup> The stress vector normal to the interface is  $T \cdot n$  with components (Fig. 2)<sup>24,30,31</sup>:

$$(T \cdot n)_z = \tau_{rz} n_r + \tau_{zz} n_z \tag{20}$$

$$(T \cdot n)_r = \tau_{rr} n_r + \tau_{rz} n_z \tag{21}$$

where

$$n_z = -R'(1 + R'^2)^{-1/2} \tag{22}$$

$$n_r = (1 + R'^2)^{-1/2} \tag{23}$$

R and R' can be either  $R_i$  and  $R'_i$  or  $R_o$  and  $R'_o$  dependent on the choice of inner or external interface. Taking the drag force  $(F_d)$  and surface tension force  $(\sigma)$  into the consideration, one can derive the following equations for the stress balance at interfaces<sup>20,21,23,30</sup>:

$$\sigma \left(\frac{1}{\mathcal{R}_L} + \frac{1}{\mathcal{R}_H}\right) n_r = \tau_{rr} n_r + \tau_{rz} n_z + F_d n_z \quad (24)$$

$$\sigma \left(\frac{1}{\Re_L} + \frac{1}{\Re_H}\right) n_z = \tau_{rz} n_r + \tau_{zz} n_z + F_d n_r \quad (25)$$

Depending on which interface is considered,  $\mathcal{R}_L$  may be either  $\mathcal{R}_{i,H}$  or  $\mathcal{R}_{o,L}$  [they are radii of the inner and outer skin curvatures in the  $(\xi_2, \xi_3)$ plane, shown in Fig. 2, respectively]. So  $\mathcal{R}_L$  can be either  $\mathcal{R}_{i,H}$  or  $\mathcal{R}_{o,H}$  [radii of the inner and outer skin curvatures in the  $(\xi_1, \xi_2)$  plane, respectively]. The relationship between  $\mathcal{R}$  and R can be expressed as follows for both inner and outer skin curvatures<sup>30,31</sup>:

$$\Re_{H}(z) = R(z) \left[ 1 + \left( \frac{dR}{dz} \right)^{2} \right]^{0.5} = R \sec \theta$$
(26)

$$\Re_L(z) = \frac{-\left[1 + \left(\frac{dR}{dz}\right)^2\right]^{1.5}}{\frac{d^2R}{dz^2}} = -\frac{\sec^3\theta}{\frac{d^2R}{dz^2}} \quad (27)$$

Substituting eqs. (22) and (23) into eq. (25) yields the stress balance equations at the external and internal skins.

$$\tau_{rz} - R'_{i}\tau_{zz} = -F_{i,d} - \sigma_{i} \left(\frac{1}{\Re_{i,H}} + \frac{1}{\Re_{i,L}}\right) R'_{i} \quad (28)$$

$$\tau_{rz} - R'_o \tau_{zz} = -F_{o,d} - \sigma_o \left(\frac{1}{\mathcal{R}_{o,H}} + \frac{1}{\mathcal{R}_{o,L}}\right) R'_o \quad (29)$$

These two equations may be rewritten as follows  $^{19-21,29}$ :

$$[\tau_{rz} - r' \tau_{zz}]_{r=R_i} = -F_{i,d} - H_i \sigma_i R'_i$$
$$= -\rho_b [\bar{\nu}_{b,z} - \bar{\nu}_{h,z}]^2 f_i - H_i \sigma_i R'_i \quad (30)$$

$$[\tau_{rz} - r'\tau_{zz}]_{r=R_o} = -F_{o,d} - H_o\sigma_o R'_o$$
$$= -\rho_a \bar{\nu}_{h,z}^2 f_o - H_o\sigma_o R'_o \quad (31)$$

Where  $\rho_a$  and  $\rho_b$  are the density of ambient air and bore fluid, respectively.  $f_o$  and  $f_i$  are drag friction coefficients at the external and internal surfaces, respectively.  $H_i$  and  $H_o$  are the combined reciprocal radii of the curvatures at the inner and outer skins, respectively, and they can be expressed as follows:

$$H_{i} = \left(\frac{1}{\mathcal{R}_{i,H}} + \frac{1}{\mathcal{R}_{i,L}}\right) = \frac{1}{R_{i}[1 + (R_{i}')^{2}]^{1/2}} - \frac{R_{i}''}{[1 + (R_{i}')^{2}]^{3/2}}$$
(32)

$$H_{o} = \left(\frac{1}{\mathcal{R}_{o,H}} + \frac{1}{\mathcal{R}_{o,L}}\right) = \frac{1}{R_{o}[1 + (R_{o}')^{2}]^{1/2}} - \frac{R_{o}''}{[1 + (R_{o}')^{2}]^{3/2}}$$
(33)

With the aid of eqs. (13), (30), and (31), eq. (14) may be expressed as

$$\begin{split} \bar{\nu}_{h,z} & \frac{\partial \bar{\nu}_{h,z}}{\partial z} = g - \frac{1}{\rho_h} \frac{\partial p}{\partial z} + \bar{\nu}_{h,z} \frac{\partial}{\partial z} \left( \frac{\bar{\tau}_{zz}}{\rho_h \bar{\nu}_{h,z}} \right) \\ & + \frac{2}{\rho_h (R_o^2 - R_i^2)} \left[ R_i (\rho_b [\bar{\nu}_{b,z} - \bar{\nu}_{h,z}]^2 f_i \right. \\ & + H_i \sigma_i R_i') - R_o (\rho_a \bar{\nu}_{h,z}^2 f_o + H_o \sigma_o R_o') \right] \quad (34) \end{split}$$

where

$$\bar{\tau}_{zz} = \frac{\int_{R_i}^{R_o} 2\pi \tau_{zz} r \ dr}{\pi (R_o^2 - R_i^2)}$$
(35)

Equation (34) describes the key parameters affecting the velocity,  $\bar{\nu}_{h,z}$ , or elongation rate,  $\partial \bar{\nu}_{h,z} / \partial z$ , of a nascent fiber during its formation. Generally, gravity g, average spinning-line stress  $\bar{\tau}_{zz}$ , and its gradient  $\partial \bar{\tau}_{zz} / \partial z$ , and the last two terms of eq. (34) play more important roles than the others.<sup>10,12,13,18</sup> This argument is due to the fact that the dense (selective) layer is usually located at the outer skin, and the inner skin is usually porous to reduce substructure resistance. As a result, the outer skin bears more stress load than the inner skin; and the elongational stress, drag, and surface tension force would compete with one another to influence the molecular orientation and chain packing of the outer skin during its formation. In case the inner skin is porous, the elongational, drag, and surface tension forces generally affect its morphology in terms of macroporous structure and mechanical strength, rather than on membrane separation performance. As a result, eq. (34) can be rewritten as follows:

$$\bar{\nu}_{h,z} \frac{\partial \bar{\nu}_{h,z}}{\partial z} = g + \bar{\nu}_{h,z} \frac{\partial}{\partial z} \left( \frac{\bar{\tau}_{zz}}{\rho_h \bar{\nu}_{h,z}} \right) - \frac{2R_o(\rho_a \bar{\nu}_{h,z}^2 f_o + H_o \sigma_o R'_o)}{\rho_h (R_o^2 - R_i^2)} \quad (36)$$

The most difficult part of solving eq. (36) is how to express the spinning-line stress  $\bar{\tau}_{zz}$  as a function of rheological parameters of a spinning solution during the hardening process, where solvent/nonsolvent coagulation occurs simultaneously.<sup>18–21</sup> The elongational viscosity depends not only on the rate of elongation, but also on the concentration of solvent as well as nonsolvent in an elongating hollow fiber. For example, Han and Segal proposed the following simple equation to relate the elongational stress and viscosity on solvent concentration during the hardening (coagulation) stage:<sup>20</sup>

$$\eta_E(\dot{\gamma}_E, C_h^s) = F(\dot{\gamma}_E)G(C_h^s) \tag{37}$$

In our case, *G* may be a complicated function that relates the effects of decreasing solvent concentration, as well as increasing nonsolvent concentration on viscosity. Thus, the relationship between  $\bar{\tau}_{zz}$  and  $\eta_E$  may be expressed as:

$$\begin{split} \bar{\tau}_{zz} &\approx \bar{\tau}_{zz} - \bar{\tau}_{rr} \approx \bar{\tau}_{zz} - P_o = \eta_E (\dot{\gamma}_E, \ C_h^s) \ \frac{d\bar{\nu}_{h,z}}{dz} \\ &= F(\dot{\gamma}_E) G(C_h^s) \ \frac{d\bar{\nu}_{h,z}}{dz} \end{split} \tag{38}$$

where  $P_o$  is atmospheric pressure. For a Newtonian fluid, eq. (38) becomes

$$\bar{\tau}_{zz} \approx \bar{\tau}_{zz} - \bar{\tau}_{rr} \approx 3\eta_E G(C_h^s) \frac{d\,\bar{\nu}_{h,z}}{dz}$$
(39)

In reality, it is not trivial to obtain G as a function of concentration. Generally, one tends to use experiments to prove qualitatively the importance of air-gap effect on membrane morphology and separation performance, and this is the approach that we would adopt in this study. The aforementioned mathematical equations will be used as the bases to explain our experimental observation.

#### **Prediction of Fiber Dimensions**

In most cases, the macrodimension (not microdimension) of a nascent hollow fiber membrane may be finalized once it immerses in an outer coagulation bath if the outer coagulant is powerful. This happens if there is a significant difference in solubility parameters between the spinning dope and outer coagulant and if the spin-line or elongational stress is low. Can one therefore predict fiber dimension in this circumstance? Using the previous assumptions, plus two new assumptions [(1) bore fluid is Newtonian and (2) end effects are neglected], one may obtain the following momentum equation of the bore fluid in the air-gap region:

$$\frac{d}{dr}\left(r\tau_{rz}^{b}\right) = \left(\frac{dp}{dz} - \rho_{b}g\right)r \tag{40}$$

where

$$\tau_{rz}^{b} = \mu_{b} \frac{d\nu_{b,z}}{dr} \tag{41}$$

with the boundary conditions:

(i) at 
$$r = R_i, \ \nu_{b,z} = \nu_{h,z,r=R_i}$$
 (42)

(ii) at 
$$r = 0, \ \tau_{rz}^b = 0$$
 (43)

The neglect of the entrance length effect is due to the fact that the entrance length for a Newtonian fluid flowing into a tube and developing a parabolic profile may be expressed as follows<sup>29</sup>:

$$L_e = 0.035 \ d_s \, \text{Re}$$

One can therefore estimate the value of  $L_e$ . For example, in our case,  $d_s = 0.045$  cm;  $V_b = 0.00417$ cm<sup>3</sup> s<sup>-1</sup>;  $\mu_b = 0.9$  cp (25°C; water)<sup>32</sup>;  $\rho_b = 1.0$  g cm<sup>-3</sup> (25°C; water)<sup>32</sup>: then

$$Re = \frac{\rho_b \nu_b d_s}{\mu_b} = \frac{4\rho_b V_b}{\pi \mu_b d_s}$$
$$= \frac{4 \times 1.0 \times 0.00417}{\pi \times 0.9 \times 10^{-2} \times 0.045} = 13.1$$

$$L_e = 0.035 imes 0.045 imes 13.1 = 0.021 ext{ cm}$$

Therefore, the flow of the bore fluid is laminar, and the end effects may be neglected. Hence, the velocity distribution of the bore fluid may be written as follows,

$$\nu_{b,z} = -\frac{1}{4\mu_b} \left( \frac{dp}{dz} - \rho_b g \right) R_i^2 \\ \times \left[ 1 - \left( \frac{r}{R_i} \right)^2 \right] + \nu_{h,z,r=R_i} \quad (44)$$

and the volume flow rate,  $V_b$ , may be expressed as

$$V_b = \pi R_i^2 \bar{\nu}_{b,z} = -\frac{\pi}{8\mu_b} \left( \frac{dP}{dz} - \rho_b g \right) \\ \times R_i^4 + \pi R_i^2 \nu_{h,z,r=R_i} \quad (45)$$

Except near the exit of a spinneret, the first term in the right-hand side of eq. (45) can be omitted in the air-gap region because its value is much smaller than that of the second term. Negligence is due to the fact that  $R_i$  in conventional hollow fibers is very small (0.1–0.5 mm), and its fourth order is therefore negligible. In addition,

 $rac{\pi R_i^2 
u_{h,z,r=R_i}}{rac{\pi 
ho_b g R_i^4}{8 \mu_i}} pprox rac{\pi R_i^2 ar 
u_{h,z}}{8 \mu_i} pprox 61 \sim 161 \gg 1$ 

dP/dz of the bore fluid may be negligible because of atmospheric surroundings. Using previous

 $\mathbf{S0}$ 

data, we calculate that

$$V_b \approx \pi R_i^2 \nu_{h,z,r=R_i} \approx \pi R_i^2 \bar{\nu}_{h,z} \tag{46}$$

One can therefore predict the inner diameter  $(D_i)$  of hollow fiber as follows,

$$D_{i} = 2R_{i} = 2\left(\frac{V_{b}}{\pi\nu_{h,L}}\right)^{1/2}$$
(47)

where  $\nu_{h,L}$  is the  $\bar{\nu}_{h,z}$  at z = L. Because we assume that a very strong coagulation occurs at external fiber surface and fiber macrodimension (not microdimension) almost immediately solidifies once it immerses in the outer coagulation bath. The following equation can be derived for the outer diameter  $(D_o)$  at z = L by rearranging eq. (22):

$$D_{o} = 2R_{o} = 2\left[\frac{\rho_{h}V_{b} + Q_{hw}}{\pi\rho_{h}\nu_{h,L}}\right]^{1/2}$$
(48)

Thus, the relationship between  $D_o$  and  $D_i$  becomes

$$\frac{D_o^2}{4} = \frac{D_i^2}{4} + \frac{Q_{hw}}{\pi \rho_h \nu_{h,L}}$$
(49)

and their ratio may be determined as follows:

$$\frac{D_o}{D_i} = \frac{R_o}{R_i} = \sqrt{1 + \frac{\rho_b}{\rho_h} \left(\frac{Q_{hw}}{Q_{bw}}\right)}$$
(50)

where  $Q_{bw} = V_b \rho_b$ . Equation (50) has been derived by Lipscomb for a melt spinning process.<sup>24</sup>

### **EXPERIMENTS**

#### **Materials and Blend Dope Solution**

PBI dope of 25.6 wt % PBI with 2 wt % LiCl in N,N-dimethylacetamide (DMAc) was purchased from the Hoechst Celanese Corporation, whereas aromatic PEI (Ultem 1010) produced from GE Plastics was used. The former has a glass transition temperature ( $T_g$ ) ~ 435°C,<sup>26–28</sup> whereas the latter has a  $T_g$  of 217°C. Solution blends of PBI and PEI were prepared in DMAc. Extensive studies have proved that PBI and PEI form fully miscibility blends and are good fiber spinning materials.<sup>25–28</sup> A PBI dope of 25.6 wt % PBI with 2 wt % LiCl in DMAc was solution-blended with a PEI dope (25.6 wt % solids in DMAc) at 20 : 80 PBI : PEI mass ratio. The calculated dope solution density ( $\rho_h$ ) is ~ 1.01 g cm<sup>-3</sup>, which is very close to the water (external coagulant).

#### **Hollow Fiber Membrane Fabrication and Tests**

The formulated blend dope was spun using the hollow fiber spinning technology described elsewhere.<sup>12,16,28</sup> Figure 1 illustrates the hollow fiber spinning apparatus used in this study. After the hollow fibers were formed, they were stored in a water bath for at least 1 day and then transferred to a tank containing fresh methanol for at least 1 h to allow sufficient solvent exchange and air-dried for at least 1 day at 25°C. Table I summarizes the spinning conditions. Membranes were fabricated as modules and tested for gas separation tests as described in the previous work.<sup>12,16,28</sup> Each module consisted of four fibers with a length of 10 cm. One end of the bundles was sealed with a 5-min rapidsolidified epoxy resin (Araldite<sup>®</sup>, Switzerland), whereas the shell side of the other end was glued onto an aluminum holder using a normal-solidified epoxy resin (Eposet<sup>®</sup>). These modules were left overnight for curing before tests. In short, the prepared module was fitted into a stainless-steel pressure cell for gas permeation measurement (pure gases: helium, hydrogen, oxygen, and nitrogen) at 100 psi (7.8 bar) and at room temperature. Gas permeation flux was measured using a flowmeter (Marheson<sup>®</sup>, Gas Products, Inc.) and a bubble flowmeter. Tensile properties of hollow fiber membranes were measured at a 50-mm gauge length with a speed of 50 mm  $min^{-1}$  using an Instron test unit (model: Instron 5542). The test method was based on ASTM measurements. At least five samples were tests for each data point.

	Spinning
Process Parameter	Condition
Spinning polymer solution	PBI/PEI/DMAc
Polymer concentration	25.6 wt % (20 : 80 PBI : PEI)
Viscosity at 25°C	6600 ср
Spinneret OD/ID	0.085 cm/0.045 cm
Spinneret temperature	Room temperature
Bore fluid	Water
Bore fluid rate	$0.00417 \ {\rm cm^3 \ s^{-1}}$
Dope pressure	20 psi
Dope flow rate	$0.0142~{ m g~s^{-1}}$
External coagulant	Water
External coagulant temperature	Room temperature
Room relative humidity	73%
Range of air-gap distance	0–30 cm
Take-up velocity	$3.33-4.94 \text{ cm s}^{-1}$
Drying procedure	1 day in water, 1 h
	in methanol, and
	1 day air-dry at
	room
	temperature

 Table I
 Process Parameters and Spinning

 Conditions of Hollow Fibers

OD, outer diameter; ID, inner diameter.

### Scanning Electron Microscopy (SEM)

Hollow fiber membrane samples for SEM study were first immersed in liquid nitrogen and fractured, and then sputtered with gold using Jeol JFC-1100E Ion Sputtering Device. A field emission scanning electron microscope Hitachi<sup>®</sup> S-4100 electron microscope was used for the investigation of hollow fiber morphology.

# Measurement of $T_g$ and Coefficient of Thermal Expansion (CTE)

All thermomechanical analyzer (TMA) samples measured herein have been immersed and rinsed in methanol for 1 h to remove any residual DMAc in the testing samples. This is due to the known fact that residual DMAC may affect the  $T_{\sigma}$ .<sup>40</sup>

After vacuum-drying at 160°C under vacuum for 24 h, the glass transitional temperatures of the hollow fibers were measured using the TMA 2940 (Waters Corporation), with a heating rate of 5°C min<sup>-1</sup> and a force of 0.05N from room temperature to 340°C. Hollow fiber samples were cut into the length of ~ 35 mm length and loaded on the TMA 2940 instrument. The onset temperature was chosen to define  $T_g$  in these measure-

Air-Gap Distance (cm)	<i>D</i> <sub>o</sub> (cm)	$D_i$ (cm)	$D_o/D_i$ Ratio (experimental)	$D_o/D_i$ Ratio [calculated from eq. (50)]	Ratio of Cross-Section Area <sup>a</sup>
0	0.082	0.040	2.05	2.09	0.99
10	0.075	0.038	1.97	2.09	0.80
20	0.068	0.035	1.94	2.09	0.65
30	0.065	0.030	2.17	2.09	0.64

Table II Dimensional Change of Hollow Fibers as a Function of Air-Gap Distance

<sup>a</sup> Cross-section area ratio of a fiber to the spinneret.

ments. The CTE of the hollow fiber was obtained from 60° to 100°C. At least two tests were conducted for each data point.

## **RESULTS AND DISCUSSION**

## Effects of Air-Gap Distance on Hollow Fiber Structure and Performance

Table II summarizes the fiber dimensional change with the air-gap distance. The ratio of the cross-section area is defined as the ratio of the cross-section area of a hollow fiber to that of the spinneret used for hollow fiber spinning. Clearly, air-gap distance plays a very important effect on the cross-section area of nascent fibers. Both the inner and outer diameters ( $D_i$  and  $D_o$ ) of dry-jet wet-spun fibers decrease with an increase in air-gap distance. The cross-section area change ratio of wet-spun fibers is close to 1 because of lack of draw down. Once there is an air gap, it induces an elongational stress on fibers because of gravity [see eq. (36)].

The calculated  $D_i$ ,  $D_o$ , and their ratios using eqs. (47) and (48) are shown in Table III and compared with the measured data of  $D_i$  and  $D_o$ .

Table III Predicted Values of Inner Diameter  $(D_i)$  and Outer Diameter  $(D_o)$ , Compared with the Measured Values

Air-Gap		Measured Value (cm)		Predicted Value (cm)	
(cm)	$\stackrel{\nu_{h,L}}{(\mathrm{cm \ s}^{-1})}$	$D_i$	$D_o$	$D_i$	$D_o$
0	3.33	0.040	0.082	0.040	0.084
10	3.47	0.038	0.075	0.039	0.082
20	4.32	0.035	0.068	0.035	0.073
30	4.94	0.030	0.065	0.033	0.069

The agreement is surprisingly good. These results show that eqs. (47) and (48) are simple, but are quite practical. The  $D_o/D_i$  ratio seems to be independent of the air-gap distance, as predicted in eq. (50).

Figures 3–5 show the cross-section morphology of hollow fibers spun with different air-gap distances. Clearly, one can see the effect of air-gap distance on the fiber cross-section morphology. Fibers spun with a greater air-gap distance have a bigger porosity closed to the external layer, whereas fibers spun with no air-gap distance seem to have the similar tight structure closed to the inner and outer surfaces. For readers' information, the dense selective layer for dry-jet wetspun fibers is located at the inner skin in our case because water is a very powerful coagulant. The porosity that appeared near the outer skin might be due to the elongational stress induced by gravity and take-up unit along the spinning line [eq. (34)]. The stress has positive or negative effects on membrane formation and performance. A high elongational stress may pull molecular chains or phase-separated domains apart in the early stage of phase separation and create porosity, whereas a medium stress may induce molecular orientation and reduce membrane porosity or free volume. If the surroundings are humid air, the situation becomes more complicated. The external surface contacts with the air first and goes through a humid-induced phase-separation process and the condensed moisture also changes the surface tension [see eq. (34)]. As a result, the elongational stress may induce orientation and reduce membrane porosity or free volume at the inner or selective skin, whereas pull molecular chains or phase-separated domains apart at the outer humid-induced phase separation or loose skin in the early stage of phase separation and create porosity.



**Figure 3** Cross-section morphology of hollow fibers spun with different air-gap distances. (Magnification: 500×; top: left—0 cm, right—10 cm; bottom: left—20 cm, right—30 cm.)

Table IV shows the observed permeance decreasing with an increase in air-gap distance. This is in agreement with our expectation. Similar phenomenon has been reported on the polyethersulfone (PES) fiber.<sup>12</sup> However, the difference between the present and the previous cases is that the dense layer location of the previous case was located at the outer skin, whereas that in the present study is located at the inner skin. For both cases, experimental data suggest that an increase in air-gap distance may result in the selective layer (no matter whether the inner or outer layer) with a greater orientation and tighter molecular packing. Because hydrogen has a linear molecule, helium has a spherical one. The former can diffuse through the inner skin layer faster than that of helium. The low permeance of these samples is also due to the fact that PBI is a good barrier material.

Table IV also summarizes the separation performance of the as-spun membranes at room temperature. Within experimental errors, both helium/hydrogen and hydrogen/nitrogen selectivities increase with an increase in air-gap distance. Al-



**Figure 4** Enlarged cross-section morphology of hollow fibers spun with different air-gap distances near the inner layer. (Magnification:  $20,000\times$ ; top: left-0 cm, right-10 cm; bottom: left-20 cm, right-30 cm.)

though a big air gap induces defects in the external surfaces as shown in Figure 6, it also results in a tighter and higher perfect inner layer (Fig. 7), which functions to enhance selectivity. The inner surfaces of different air-gap distances also confirm our hypothesis.

## Effects of Air-Gap Distance on Mechanical Properties

Table V shows the mechanical properties of 20 : 80 PBI/PEI hollow fibers vary with air-gap dis-

tances. Within the experimental error, both the tensile strength and elongation at break seem to be independent of air-gap distances, except at 30 cm. For an air-gap distance of 30 cm, the external skin defects result in a significant drop on both tensile strength and elongation at break. However, the relationship between tensile modulus and air-gap distance is interesting. In the beginning, modulus increases with air-gap distance and then decreases with the distance. This phenomenon is agreement with expectation that airgap distance has duel effects.



**Figure 5** Enlarged cross-section morphology of hollow fibers spun with different air-gap distances near the outer layer. (Magnification:  $20,000\times$ ; top: left—0 cm, right—10 cm; bottom: left—20 cm, right—30 cm.)

## Effects of Air-Gap Distance on $T_g$ s and CTE of Hollow Fibers

 $T_g$  is defined as the temperature above which the majority of bonds in polymeric chains have acquired sufficient thermal energy for rotational motion, or considerable torsional oscillation. Below the  $T_g$ , the mobility of polymeric chains is so drastically reduced that the majority of polymeric chains have fixed conformations.  $T_g$  also is the temperature at which the thermal expansion coefficient changes in going from the rubbery to the glassy state.<sup>38,39</sup> Generally, a rapid-quenched polymer possess a higher free volume and exhibits a higher  $T_g$  than one quenched at a slower rate.<sup>11</sup> The phase inversion process that occurred in the formation of a nascent hollow fiber has a similar trend. Any acceleration on fiber coagulation (quench) rate may result in similar effects on  $T_g$ . Figure 8 illustrates the typical TMA curves for 20 : 80 PBI : PEI dry-jet wet-spun hollow fibers. Table VI summarizes the  $T_g$  change as a function of

		$(P/L)_I (\text{GPU})^{\mathrm{a}}$			Selectivity		
Air-Gap Distance (cm)	$O_2$	$N_2$	He	$H_2$	O <sub>2</sub> /N <sub>2</sub>	$He/N_2$	$H_2/N_2$
0	2.62	2.68	38.8	69.4	0.98	14.5	25.9
10	2.40	2.50	37.8	62.0	0.96	15.1	24.8
20	2.10	2.21	35.7	60.8	0.95	16.2	27.5
30	1.13	1.17	27.3	48.3	0.97	23.3	41.3

Table IVEffect of Air-Gap Distance on the Gas Separation Performance of PBI : PEI Blend HollowFiber Membranes Using Water as the Bore Fluid

 $^{\rm a}~{\rm GPU}$  = 1  $\times$  10  $^{-6}~{\rm cm}^3$  (STP)  ${\rm cm}^{-2}~{\rm cm}^{-1}~{\rm Hg}^{-1}~{\rm s}^{-1}.$ 



**Figure 6** External skin morphology of hollow fibers spun with different air-gap distances. (Magnification: 35,000×; top: left—0 cm, right—10 cm; bottom: left—20 cm, right—30 cm.)

5.0 kV x35.0K

857 nm

857nm

5.0 kV x35.0K



**Figure 7** Internal skin morphology of hollow fibers spun with different air-gap distances. (Magnification: 35,000×; top: left—0 cm, right—10 cm; bottom: left—20 cm, right—30 cm.)

air-gap distance for PBI/PEI membranes using water as the bore fluid.  $T_g$  data suggest that an increase in air-gap distance result in a decrease in the  $T_g$ . This is due to that fact that a dry-jet wet-spun fiber has a much slower coagulation rate during the air-gap region. Besides, the orientation introduces into nascent hollow fiber because of an elongational stress [see eq. (36)]. As a result, they have different responses during the TMA measurements. The slow compacted dry-jet wet-spun fibers have a structure closer to the equilibrium molecular packing state than the rapidly quenched wet-spun fibers. An increase in air-gap distance probably results in a decrease of hollow fiber free volume. Therefore, the former has a  $T_g$  lower than that of the latter. Similar results have been reported on PES fibers.<sup>12</sup> Table VI also illustrates the effect of air-gap distance on fiber CTEs and shows the calculated CTE of these hollow fibers decreases with increasing air-gap distance. There are probably two dominant mechanisms

Air-Gap Distance (cm)	Break Strength (Mpa)	Elongation at Break (%)	Young's Modulus <sup>a</sup> (MPa)
0	$10.2\pm0.28$	$18.9\pm2.97$	$312 \pm 8.4$
10	$9.8\pm0.27$	$13.3\pm2.23$	$343\pm8.6$
20	$10.5\pm0.33$	$14.1\pm2.76$	$374\pm16.8$
30	$8.7\pm0.64$	$7.6\pm2.52$	$339 \pm 12.1$

Table VMechanical Properties of PBI : PEI Blend Hollow Fiber Membranes Spun from DifferentAir-Gap Distances

<sup>a</sup> Young's modulus calculated on the strain channel with a lower bound value of 0.5% and an upper bound value of 1.0%.

to induce molecular orientation during the phase inversion of fiber formation. This result is in agreement with previous work that an increase in draw ratio or molecular orientation results in a decrease in CTE.<sup>17,32–34</sup>

### **CONCLUSIONS**

We have derived the basic equations to describe the velocity profile of a nascent hollow fiber in the air-gap region as a function of gravity, mass transfer, surface tension, drag forces, spinning stress, and rheological parameters of spinning solutions. Experimental data, such as SEM micrographs, gas separation performance, and CTE based on hollow fiber membranes spun from 20 : 80 PBI/PEI dopes with different air-gap distances—qualitatively support the validity of the mathematical model. We also derived two simple equations to predict the inner and outer diame-



**Figure 8** A typical TMA curve showing the analysis of the CTE and  $T_g$  (20 : 80 PBI : PEI hollow fibers spun from an air-gap distance of 20 cm using water as the bore fluid; vacuum-dried temperature: 160°C).

Air-Gap Distance (cm)	$(\mu m m^{-1} °C^{-1})$	$\begin{array}{c} T_g \\ (^{\circ}\mathrm{C}) \end{array}$
0	48.9	253.3
10	50.4	249.6
20	48.6	247.8
30	47.7	245.1

Table VI CTEs, and  $T_g$ s of PBI : PEI Blend Membranes Spun from Different Air-Gap **Distances (Vacuum-Dried Temperature: 160°C** for 24 hours)

ters of hollow fibers, and the predicted values are very close to the experimental results.

Spin-line stress may have positive or negative effects on membrane formation and separation performance, depending on the process conditions. A high elongational stress may pull molecular chains or phase-separated domains apart in the early stage of phase separation and create porosity, whereas a medium stress may induce molecular orientation and reduce membrane porosity or free volume. As a result,  $T_g$  of dry-jet wet-spun fibers may be lower than that of wetspun fibers, and  $T_{g}$  decreases with an increase in air-gap distance. This conclusion is valid no matter whether the selective layer is located in either the inner or outer skin.

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#### NOMENCLATURE

#### Symbols

$C_h^s$	solvent concentration in a nascent hol-
	low fiber (g $cm^{-3}$ )
$\bar{C}^s_b$	average solvent concentration of bore
	fluid (g cm $^{-3}$ )
$\bar{C}_{h}^{s}$	average solvent concentration in a nas-
	cent hollow fiber $(g \text{ cm}^{-3})$
$d_s$	inner tube diameter of spinneret (cm)
$D_i$	inner diameter of hollow fiber (cm)
$D_o$	outer diameter of hollow fiber (cm)
$D_{sp}$	diffusion coefficient of solvent in a nas-
- 1	cent hollow fiber (cm <sup>2</sup> s <sup>-1</sup> )
$f_o$	drag coefficient at the external surface
	of a nascent hollow fiber
$f_i$	drag coefficient at the internal surface of
	a nascent hollow fiber

$$\begin{array}{ll} F(\dot{\gamma}_E) & \text{material function defined [eq. (37)]} \\ F_d & \text{drag force (dyn)} \\ g & \text{gravitational constant (980 cm s}^{-2}) \\ G(C_h^s) & \text{material function defined [eq. (37)]} \\ H_i & \text{the combined reciprocal radii of the cur-} \end{array}$$

vatures at the inner skin of the nascent hollow fiber  $(cm^{-1})$ 

- $H_o$ the combined reciprocal radii of the curvatures at the outer skin of the nascent hollow fiber  $(cm^{-1})$
- mass transfer coefficient of solvent at  $k_i$ the inner interface (cm  $s^{-1}$ )
- L air-gap distance (cm)

g

r

- entrance length (cm)  $L_e$
- Defined in Figure 1 and eq. (23) $n_r$
- Defined in Figure 1 and eq. (22) $n_z$
- mass flow rate of dope solution  $(g s^{-1})$  $Q_{hw}$
- mass flow rate of bore fluid (g  $s^{-1}$ )  $Q_{bw}$
- Р atmospheric pressure (Pa)
  - horizontal position coordinate relative to the center of a nascent hollow fiber (cm)
- r'the first derivative of r with respect to z[eq. (18)]
- inner radius of a nascent hollow fiber  $R_i$ (cm)
- outer radius of a nascent hollow fiber  $R_o$ (cm)
- Re Reynolds number
- $R'_i, R'_o$ the first derivative of  $R_i$  and  $R_o$ , with respect to z, respectively
- $R''_{i}, R''_{o}$ the second derivative of  $R_i$  and  $R_o$ , with respect to z, respectively
- $\mathcal{R}_H$ radius of skin curvatures in the  $(\xi_1, \xi_2)$ plane [defined in eqs. (26) and (27) and Fig. 1]
- $\Re_L$ radius of skin curvatures in the  $(\xi_2, \xi_3)$ plane [defined in eqs. (26) and (27) and Fig. 1]
  - glass transition temperature (°C)

volume flow of the bore fluid  $(\text{cm}^3 \text{ s}^{-1})$ 

permeance of hollow fiber membrane to gas *i* (GPU, 1 GPU =  $1 \times 10^{-6}$  cm<sup>3</sup>  $(STP) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1})$ 

### Greek

α

 $\alpha_{i/j}$ 

 $\sigma_i$ 

 $\sigma_o$ 

 $T_g V_b$ 

 $\left(\frac{P}{l}\right)_{l}$ 

- CTE ( $\mu$ m m<sup>-1</sup> °C<sup>-1</sup>)
- selectivity of gas *i* over gas *j* surface tension at bore fluid-nascent
- hollow fiber interface (dyne  $cm^{-1}$ )
- surface tension at air and nascent hollow fiber interface (dyne  $cm^{-1}$ )

$\mu_b$	viscosity of the bore fluid (cp)
$\dot{\gamma}_E$	strain rate or rate of elongation $(s^{-1})$
$\eta_E$	elongational viscosity
$\nu_b$	average velocity of the bore fluid in the inner tube of spinneret (cm $s^{-1}$ )
$v_{b,z}$	velocity of z-component of the bore fluid $(\text{cm s}^{-1})$
$\nu_{h,L}$	take-up rate of hollow fiber (cm $s^{-1}$ )
$\nu_{h,r}$	velocity of <i>r</i> -component of nascent hol- low fiber (cm s <sup>-1</sup> )
$\nu_{h,z}$	velocity of z-component of nascent hollow fiber (cm $\rm s^{-1})$
$v_{h,z,r=Ri}$	velocity of z-component of nascent hol- low fiber at inner skin $(r = R_i)$ (cm s <sup>-1</sup> )
$\overline{\nu}$	average velocity over the cross-section $(cm \ s^{-1})$
$\theta$	angle (Fig. 1)
$ ho_a$	density of ambient air (g cm <sup>-3</sup> )
$ ho_b$	density of the bore fluid $(g \text{ cm}^{-3})$
$ ho_h$	density of nascent hollow fiber $(g cm^{-3})$
$ au_{ii}$	extra stress (dyn $cm^{-2}$ )

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