Fundamental Analysis of the Dynamics, Mass Transfer, and Coagulation in Wet Spinning of Fibers

JAMES L. WHITE and TONY A. HANCOCK,* Polymer Engineering, The University of Tennessee, Knoxville, Tennessee 37916

Synopsis

New models are developed to analyze the wet spinning process. These involve a formulation of simultaneous overall mass, force, and solvent mass transfer balances. In the first-order model, internal concentration gradients and mass transfer resistance within the fiber are neglected. It is equivalent to the Kase-Matsuo melt spinning model. In the second-order model, concentration gradients and diffusion within the fiber are included. Comparison is made with an experimental study of wet spinning nylon-66 fibers. The first-order model seriously underpredicts final fiber diameter under conditions of specified spinline tension and spinning efflux. The second-order model gives better agreement between theory and experiment.

INTRODUCTION

Commercial synthetic fibers are produced by either melt or solution spinning processes. Melt spinning is the more rapid and efficient and polymers which may be handled in the molten state such as polyolefins, nylons, and polyester are melt spun. However, many polymers are thermally degraded below their melting temperatures, and fibers must be formed from them in solution. Indeed the first polymers formed into fibers were cellulosics, and the first patents in this area involve solution spinning.¹⁻⁴ Today acrylics and aromatic polyamides as well as cellulosics are solution spun. The filamentous solutions emerging from the spinneret may be coagulated by either a bath of liquid which extracts the solvent (wet spinning) or blowing air to evaporate it (dry spinning).

It is the purpose of the present paper to present a new analysis of the dynamics and mass transfer process occurring during wet spinning. Only a few earlier authors have turned their attention to this problem. An overall study of the dynamics of the wet spinning process was published by Brinegar and Epstein⁵ in 1967. These authors attempted to interrelate the applied tension with drag, momentum, and rheological forces on the filament. Detailed analyses of special cases are given by Han and Segal^{6,7} and Yerushalmi and Shinnar⁸ which ignore mass transfer and coagulation effects and in one case also drag^{6,7} and in the other non-Newtonian flow characteristics.⁸ The existence of nonuniform stress distributions in the filament as coagulation proceeds in the bath is discussed by Ziabicki⁹ and by McKay, Ferguson, and Hudson.¹⁰ The mass transfer process in wet spinning has received consideration from various investigators beginning in the 1940s.^{11,12} Further studies of the mass transfer process are reported by Takizawa,^{13,14} Griffith,¹⁵ Paul,¹⁶ Booth,¹⁷ Epstein and Rosenthal,¹⁸ and Hancock, White, and Spruiell.^{19,20} The latter authors¹⁹ note the occurrence of interfacial

* Present address: IBM, Lexington, KY.

Journal of Applied Polymer Science, Vol. 26, 3157–3170 (1981) © 1981 John Wiley & Sons, Inc. CCC 0021-8995/81/093157-14\$01.40 instabilities during mass transfer and its influence on coagulation. None of these studies brings together the dynamics and mass transfer processes.

There have been a number of useful studies of the related dry spinning process where mass transfer processes are of great importance. The papers of Fok and Griskey,^{21,22} Ohzawa, Nagano, and Matsuo,^{23–25} and Brezinsky, Williams, and LaNieve²⁶ are to be noted. These authors bring together combined force, heat, and mass balances. The variation of elongational viscosity with concentration is considered.

There are no general models of the interaction of dynamics and mass transfer in the wet spinning process. In the present paper, we develop a new series of models of varying sophistication of the wet spinning process. Calculations based on these models will be made and compared with experiment. The interaction of force balances and mass transfer processes are considered. Nonisothermal phenomena and energy balances are neglected.

BALANCE EQUATIONS

Overall and Polymer Phase Mass Balance

Let G be the total forward mass flux of the polymer solution filament as it moves through the bath of a coagulating phase as shown in Figure 1. It may be expressed as the sum of polymer phase G_p , solvent phase G_s , and coagulant phase (within the filament) G_n mass fluxes

$$G = G_p + G_s + G_n \tag{1}$$

If we let c be the mass fraction of solvent and c_n of the coagulating nonsolvent in the solution, we may write

$$G_s = \rho c A v \tag{2a}$$

with

$$\overline{c} = \frac{1}{A} \int c da \tag{2b}$$

$$G_p = \rho(1 - \overline{c} - \overline{c}_n), \quad G_n = \rho \overline{c}_n A v$$
 (2c)

Here ρ is mass density, A is the cross-sectional area of the fiber, and v is the linear

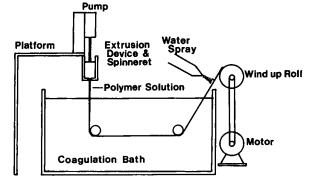


Fig. 1. Wet spinning process.

velocity. Density variations in the system are ignored. G_p is constant along the length of the filament, but G_s decreases with position from spinneret to take-up. Generally \overline{c}_n and G_n will be expected to be small.

Dynamics

The forces acting on a fiber spinline include take-up tension F_L , frictional drag $F_{\rm drag}$, gravity $F_{\rm grav}$, and momentum fluxes. If we let the x axis run along the filament, between position x and position L, a force momentum flux balance yields²⁷

$$(F_L - G_L v_L) - (F_x - G_x v_x) = F_{\text{grav}} - F_{\text{drag}}$$
(3)

Here G_L is the mass flux at position L and G_x at position x. This balance accounts for the loss in mass occurring in the spinline as the solvent dissolves in the coagulation bath.

As the fiber is largely pulled horizontally through a bath of approximately equal density. F_{grav} should be expected to be small. The velocity of fibers moving through a coagulation bath is generally small. Despite the variation of G along the threadline, values of G_v must be expected to be small. This suggests that for most applications of interest, eq. (3) reduces to

$$F_x = F_L + F_{\rm drag} \tag{4}$$

The force F_x , often called the rheological force F_{rheo} , may be expressed as the stress integrated across the cross section

$$F_{\rm rheo} = \int_0^A \sigma_{xx} da = \int_0^R 2\pi r \sigma_{xx} dr$$
 (5)

The tensile stress σ_{11} is related to the local rheological properties of the polymer solution. To a first approximation, it may be approximated through a spinline elongational viscosity χ_{sp} defined by

$$\sigma_{xx} = \chi_{\rm sp}(dv/dx) \tag{6}$$

Actually eq. (6) does little more than define χ_{sp} if the rheological behavior is more complicated than that of a viscous fluid. This is certainly the case for viscoelastic polymer solutions.

The drag force may be expressed

$$F_{\rm drag} = \int_0^L \pi d\,\sigma_f dx \tag{7}$$

where the shear stress is

$$\sigma_f = C_f \rho_{\text{ext}} v^2 / 2 \tag{8}$$

Here C_f is the friction factor. Sano and Orii²⁸ and Hamana, Matsui, and Kato²⁹ have determined the friction factor for moving threadlines. From the latter authors,

$$C_f \simeq 0.68 (dv \rho_{air}/\eta_{air})^{-0.2}$$
 (9)

where the subscript air refers to the ambient air. In wet spinning this would be replaced by the subscript *ext* for the coagulation of bath.

Mass Balance and Diffusion of Solvent

We now consider the rates of solvent loss to the coagulation bath. In general we must develop a set of diffusion equations for the solvent molecules in both the moving filament and the surrounding bath.

An overall mass balance on a moving filament has the form

$$\frac{d}{dx}\left[\rho\bar{c}Av\right] = -K\pi d(\bar{c}-c_0) \tag{10}$$

where K is an overall mass transfer coefficient and c_0 is the fraction of solvent in the coagulation bath. Equation (10) accounts for mass transfer resistance in both the fiber and bath phases. If we account for external, internal (fiber), and interfacial resistance, we may write K as

$$\frac{1}{K} = \frac{1}{k_{\text{ext}}} + \frac{1}{k_i} + \frac{1}{k_{\text{int}}}$$
(11)

where k_{ext} is the external liquid side, k_{int} the internal fiber solid side, and k_i the interfacial mass transfer coefficient.

We may eliminate v in eqs. (2c)–(10), where we neglect \overline{c}_n to give

$$\frac{d}{dx} \left[\frac{\overline{c}G_p}{(1-c)} \right] = K\pi d(\overline{c} - c_0)$$

$$\frac{G_p}{(1-\overline{c})^2} \frac{d\overline{c}}{dx} = K\pi d(\overline{c} - c_0)$$
(12)

The diffusion within the fiber is complex involving a ternery system, of polymer, solvent, and coagulant. Within the filament, diffusion processes will be governed by the diffusion equation in cylindrical coordinates. We may write radial fluxes j within the filament $as^{30,31}$

$$j_s = -D_{\text{int}} \frac{\partial c}{\partial r} + c(j_s + j_n + j_p)$$
(13a)

$$j_n = -D_{\text{int}}^n \frac{\partial c_n}{\partial r} + c_n (j_s + j_r + j_p)$$
(13b)

$$j_p = -D_{\text{int}}^p \frac{\partial c_p}{\partial r} + c_p (j_s + j_r + j_p)$$
(13c)

Different simplifications are possible. We shall take

$$j_s + j_n + j_p \cong \text{small} \tag{14}$$

and neglect the presence of nonsolvent. This leads to

$$\frac{\partial c}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}\left(rj_s\right) = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{\rm int}\frac{\partial c}{\partial r}\right)$$
(15a)

where D_{int} is the concentration dependent diffusivity of the solvent within the fiber; D_{int} will in general be larger near the center of the filament where the solvent concentration is larger and smaller near the outer skin where the polymer concentration is higher. The boundary conditions are

$$c(r,0) = c_i \tag{15b}$$

$$\frac{\partial c}{\partial r}(0,t) = 0 \tag{15c}$$

$$-D_{\rm int} \frac{\partial c}{\partial r} \left(\frac{d}{2}, t \right) = k_{\rm ext} (\bar{c} - c_0) \tag{15d}$$

FIRST-ORDER MODEL

Balance Equations

We may develop an approximate theory of the dynamics and mass transfer of the wet spinning process equivalent to the theories used to analyze the melt spinning process (see Table I). Such theories which include both dynamics and heat transfer date to Kase and Matsuo^{32,33} and Hamana, Matsui, and Kato.²⁹ They consider uniform properties across the fiber cross section and neglect heat transfer resistance within the fiber. In the problem of mass transfer in a fiber spinning process, this is equivalent to writing eqs. (4), (10), and (12) as

$$F_{\rm rheo} = \sigma_{xx}A = F_L + F_{\rm drag} \tag{16}$$

$$\frac{d}{dx}\left[\rho\bar{c}Av\right] = -k_{\rm ext}\pi d(\bar{c}-c_0) \tag{17a}$$

$$\frac{G_p}{(1-\bar{c})^2}\frac{d\bar{c}}{dx} = -k_{\text{ext}}\pi d(\bar{c}-c_0)$$
(17b)

If we can represent the tensile stress σ_{xx} in eq. (16) with eq. (6) for the spinline elongational viscosity χ_{sp} , then using Eq. (2a)

$$\sigma_{11} = \chi_{\rm sp} \frac{dv}{dx} = \chi_{\rm sp} \frac{d}{dx} \left[\frac{G_p}{\rho (1 - \bar{c})A} \right]$$
(18)

and

$$F_{\rm rheo} = -\frac{\chi_{\rm sp}G_p}{\rho(1-\bar{c})}\frac{1}{A}\frac{dA}{dx} - \frac{\chi_{\rm sp}G_p}{\rho(1-\bar{c})^2}\frac{d\bar{c}}{dx}$$
(19)

Equations (16) and (19) represent the force balance equation in this approximation and eq. (17b) the mass balance on solvent.

TABLE I							
Approximations of Models of This Paper							

Model	External mass transfer resistance	Radial concen- tration gradient	Internal mass transfer resistance	Diffusion of	Radial variatior of rheological properties of filament	Influence of radial properties variations of solvent diffusity
First order Second	· included	neglected	neglected	neglected	neglected	
order	included	included	included	included	included	neglected

Placing our balances in dimensionless form, we have

$$(1-\bar{c})\,\frac{(F_L+F_{\rm drag})\rho d_0}{\chi_0 G_p} \left(\frac{\chi_0}{\chi_{\rm sp}}\right) = -2\,\frac{d\ln d^*}{dx^*} - \frac{1}{(1-\bar{c})}\,\frac{d\bar{c}}{dx^*} \tag{20}$$

$$\frac{1}{(\overline{c}-c_0)(1-\overline{c})^2}\frac{d\overline{c}}{dx^*} = -\pi \left(\frac{k_{\text{ext}}d_0^2\rho}{G_p}\right)d^* = -\pi \left(\frac{k_{\text{ext}}d_0}{\mathcal{D}_{\text{ext}}}\right)\left(\frac{\rho d_0\mathcal{D}_{\text{ext}}}{G_p}\right)d^*, \quad (21)$$

where χ_0 is the initial spinline viscosity at the capillary and d_0 the initial fiber diameter. x^* is x_1/d_0 and d^* is d/d_0 .

We find that $d^*(x^*)$ and $\overline{c}(x^*)$ depend upon the dimensionless groups

$$\frac{F_L\rho d_0}{\chi_0 G_p}, \quad \frac{F_{\rm drag}\rho d_0}{\chi_0 G_p} \quad \left({\rm or} \, \frac{\pi d_0^2 \rho^2 v^2 L}{\chi_0 G_p} \quad {\rm and} \quad \frac{dv \rho_{\rm ext}}{\eta_{\rm ext}} \right), \quad \frac{k_{\rm ext} d_0}{\mathcal{D}_{\rm ext}}, \quad \frac{G_p}{\rho d_0 \mathcal{D}_{\rm ext}}, \quad \frac{\chi_{\rm sp}}{\chi_0}$$

The quantity $k_{\text{ext}} d_0 / \mathcal{D}_{\text{ext}}$ is an external Sherwood number, and $G_p / \rho d_0 \mathcal{D}_{\text{ext}}$ is a diffusion Peclet number.

Before we may solve this set of equations, we need to further reduce the number of independent dimensionless groups. The ratio χ_{sp}/χ_0 represents the concentration dependence of the spinline elongational viscosity. There are really no useful studies of this for polymer solutions. However, extensive data on the concentration dependence of the *shear* viscosity is available for polymer.³⁴⁻³⁷ In most systems investigated in the literature, the zero shear viscosity varies with the fifth power

$$\frac{\chi_{\rm sp}}{\chi_0} = \left(\frac{1-\bar{c}}{1-\bar{c}_0}\right)^5 \tag{22}$$

It is through eq. (22) that we implicitly account for the occurrence of coagulation. In the next section we turn to a discussion of external mass transfer, which will allow us to eliminate the dimensionless group $k_{\text{ext}}d_0/\mathcal{D}_{\text{ext}}$.

Mass Transfer Coefficient

The external mass transfer coefficient requires evaluation. However, there appear to be no suitable experimental data in the literature. In the absence of any data we may estimate the value using the analogy between heat transfer and mass transfer.^{30,31} The most commonly used expression for the heat transfer coefficient h on a fiber spinline is that of Kase and Matsuo³² which takes the form

$$(hd/\kappa_{\rm air}) = 0.42 (dv\rho_{\rm air}/\eta_{\rm air})^{1/3}$$
 (23)

where κ_{air} is the thermal conductivity of the air.

Turning now to the mass transfer coefficient, dimensional analysis of the equations of change for diffusion suggest the form^{30,31}

$$k_{\rm ext} d / \mathcal{D}_{\rm ext} = N_{\rm Sh} = F[N_{\rm Re}, N_{\rm Sc}]$$
(24a)

$$= F\left[\frac{dv\rho_{\text{ext}}}{\eta_{\text{ext}}}, \frac{\eta_{\text{ext}}}{\rho_{\text{ext}}\mathcal{D}_{\text{ext}}}\right]$$
(24b)

where N_{Sh} , N_{Re} , and N_{Sc} are dimensionless groups defined by eqs. (24a) and (24b) which represent the Sherwood, Reynolds, and Schmidt numbers, respec-

tively. If we accept the heat transfer-mass transfer analogy, the equivalent of the Kase-Matsuo relation [eq. (23)] is

$$N_{\rm Sh} = 0.47 \, N_{\rm Re}^{1/3} \, N_{\rm Sc}^{1/3} \tag{25}$$

where we have noted that the Prandtl number (heat transfer equivalent to the Schmidt number³⁰ for air is 0.7, and, as noted by Chilton and Colburn and later investigators, the power of the Schmidt and Prandtl numbers on mass transfer correlations for Nusselt and Sherwood numbers is invariably 1/3. With the presumption of eq. (25) we specifically omit from our modeling fibers in which Marangoni-type instabilities occur during mass transfer. As noted in our previous paper,¹⁹ such phenomena commonly occur in wet spinning when there are high heats of solution between solvent and coagulant. However, they give rise to undesirable fibers containing fluted void structures.

If we accept eq. (25) for k_{ext} , it allows us to rewrite eq. (21) as

$$\frac{1}{(c-\overline{c}_0)(1-\overline{c})^2}\frac{d\overline{c}}{dx^*} = -0.47\pi \left(\frac{4}{\pi}\right)^{2/3} \left(\frac{\rho \mathcal{D}d_0}{G_p}\right)^{2/3} d^{*4/3}$$
(26)

Calculations

We have made calculations of the extent of drawdown of wet spun fibers using the model of this section. From eqs. (20), (21), (25), and (26), it follows that

$$d^* = d^* \left[\frac{F_L \rho d_0}{\chi_0 G_p}, \frac{F_{drag} \rho d_0}{\chi_0 G_p}, \frac{G_p}{\rho d_0 \mathcal{D}_{ext}} \right]$$
(27a)

or

$$d^* = d^* \left[\frac{F_L \rho d_0}{\chi_0 G_p}, \quad \frac{F_{\text{drag}} \rho d_0}{\chi_0 G_p}, \quad \frac{(k_{\text{ext}})_0 d_0}{\mathcal{D}_{\text{ext}}} \right]$$
(27b)

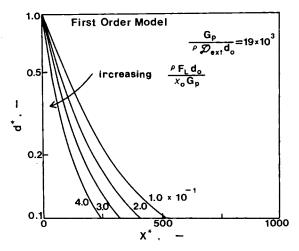


Fig. 2. Theoretical prediction of drawdown $d^*(d/d_0)$ as a function of distance from the spinneret in the bath $x^*(d/d_0)$ for the first-order model. We show the influence of increasing $\rho F_L d_0 / \chi_0 G_p$ at fixed $G_p / \rho \mathcal{D}_{ext} d_0$ of 19,000.

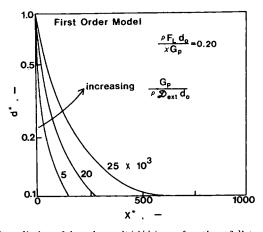


Fig. 3. Theoretical prediction of drawdown $d^*(d/d_0)$ as a function of distance from the spinneret in the bath $x^*(x/d_0)$ for the first-order model. We show the influence of increasing $G_p/\rho \mathcal{D}_{ext}d_0$ at fixed $\rho F_L d_0/\chi G_p$ of 0.20.

We have generally found that F_L considerably exceeds F_{drag} in most experiments carried out in our laboratories, and we have neglected drag here.

Calculations based on these expressions are shown in Figures 2 and 3. In Figure 2, we show d^* as a function of $F_L \rho d_0 / \chi_0 G_p$ at fixed Sherwood and Peclet numbers. For the special case of zero (k_{ext}) we have

$$d^* = \exp\{-[F_L \rho d_0 (1 - \bar{c})/2\chi_0 G_p] x^*\}$$
(28)

The dimensionless diameter decreases exponentially with drawdown. This is the classical melt spinning solution for a Newtonian fluid. A similar trend is observed in Figures 2 and 3 where near exponential behavior is observed. Increasing $k_{\text{ext}} d_0 / \mathcal{D}_{\text{ext}}$ or $(G_p / \rho d_0 \mathcal{D}_{\text{ext}})$ decreases the rate and extent of drawdown. This is clearly due to the increasing elongational viscosity of the "spinning dope" brought about by increases in polymer concentration along the spinline.

Critique

The basic problem with the model described in the previous section is that, from a scientific point of view, radial variations in the fiber are neglected and that internal resistance to mass transfer is not considered. Use of an averaged viscosity $\chi_{sp}(\bar{c})$ rather than considering the radial variation of $\chi(r)$ tends to predict a lower resistance of the filament to deformation. Neglect of internal resistance to mass transfer makes the diffusion of the solvent out of the fiber occur more rapidly.

SECOND-ORDER MODEL

Balance Equations

In this approximation we consider radial variations in polymer and solvent concentration within the fiber as well as internal mass transfer resistance. We replace eqs. (16) and (17a) with

$$F_{\rm rheo} = \left[\int_0^R 2\pi r \chi_{\rm sp}(r) dr\right] dv/dx = F_L + F_{\rm drag}$$
(29a)

$$\frac{d}{dx}\left[\rho\bar{c}Av\right] = \left(\frac{1}{k_{\text{ext}}} + \frac{1}{k_{\text{int}}}\right)^{-1} \pi d(\bar{c} - c_0)$$
(29b)

The concentration profile within the fiber is given by the diffusion equation, eq. (15a), with boundary conditions eqs. (15b)–(15d). We take in this approximation on internal diffusion that the diffusivity is constant. This solution has the form for constant R^{38}

$$\frac{c-c_0}{c_i-c_0} = 1 - \sum \left[\frac{N_{\mathrm{Sh,ext}} J_0(\beta_n r/R)}{(\beta_n^2 + N^2_{\mathrm{Sh,ext}}) J_0(\beta_n)} \right] \exp(-\beta_n^2 \mathcal{D}_{\mathrm{int}} t/R^2)$$
(30)

where $\mathcal{D}_{int}t/R^2$ is the diffusion Fourier number and β_n are the roots of

$$\beta_n J_1(\beta_n) - N_{\text{Sh,ext}} J_0(\beta_n) = 0$$
(31)

where $N_{\text{Sh,ext}}$ is $k_{\text{ext}}d/\mathcal{D}_{\text{ext}}$. The Fourier number is now a parameter of the problem.

As the fiber diameter is drawn down in the bath, i.e., R = R(t), eq. (30) is not strictly the correct solution. However, we will accept it as being valid within this second-order model.

Placing our balances in dimensionless form similar to eqs. (20) and (21)

$$\frac{(F_L + F_{\rm drag})\rho d_0}{\chi_0 G_p} \frac{1 - \bar{c}}{\int_0^{-1} 2\xi (\chi_{\rm sp}/\chi_0) d\xi} = -2 \frac{d\ln d^*}{dx} + \frac{1}{(1 - c)} \frac{d\bar{c}}{dx^*}$$
(32a)
$$\frac{1}{(\bar{c} - c_0)(1 - \bar{c})^2} \frac{d\bar{c}}{dx_1^*} = -\pi N_{\rm Sh,ext} \left(\frac{\rho d_0 \mathcal{D}_{\rm ext}}{G_p}\right) \left(1 + \frac{k_{\rm ext}}{k_{\rm int}}\right)^{-1} d^*$$
(32b)

The internal mass transfer coefficient
$$k_{int}$$
 for a cylinder may be expressed, after Giddings,³⁹ as

$$k_{\rm int} = 0.25\mathcal{D}_{\rm int}/R \tag{33}$$

We may write

$$\frac{k_{\rm ext}}{k_{\rm int}} = \frac{2N_{\rm Sh,ext}}{\mathcal{D}_{\rm int}/\mathcal{D}_{\rm ext}}$$
(34)

The external Sherwood number is given by eq. (25).

Calculations

The reduction in diameter as the fiber moves through the bath is determined by the dimensionless groups

$$d^* = d^* \left[\frac{F_L \rho D_0}{\chi_0 G_p}, \frac{F_{\text{drag}} \rho d_0}{\chi_0 G_p}, \frac{G_p}{\rho d_0 \mathcal{D}_{\text{ext}}}, \frac{\mathcal{D}_{\text{int}}}{\mathcal{D}_{\text{ext}}}, \frac{\mathcal{D}_{\text{int}} \theta}{R^2} \right]$$
(35a)

or equivalently

$$d^* = d^* \left[\frac{F_L \rho d_0}{\chi_0 G_p}, \frac{F_{\text{drag}} \rho d_0}{\chi_0 G_p}, N_{\text{Sh,ext}}, \frac{\mathcal{D}_{\text{int}}}{\mathcal{D}_{\text{ext}}}, \frac{\mathcal{D}_{\text{int}} \theta}{R^2} \right]$$
(35b)

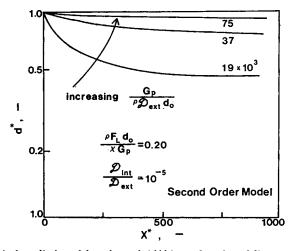


Fig. 4. Theoretical prediction of drawdown $d^*(d/d_0)$ as a function of distance from the spinneret $x^*(x/d_0)$ for the second-order model. We show the influence of increasing $G_p/\rho \mathcal{D}_{ext}d_0$ at fixed $\rho F_L d_0/\chi_0 G_p = 0.20$ and $\mathcal{D}_{int}/\mathcal{D}_{ext} = 10^{-5}$.

Here θ is a characteristic residence time in the bath.

In Figures 4, 5, and 6 we show the drawdown of d^* as a function of these dimensionless groups where we have made calculations for the case of zero drag force. First in comparison with the one-dimensional model, the drawdown is much less. As with the first-order model, the drawdown increases with increasing $F_L\rho d_0/\chi_0 G_p$ and with decreasing external Sherwood number. The drawdown also increases with decreasing $\mathcal{D}_{int}/\mathcal{D}_{ext}$.

An important parameter which is not noted explicitly in eq. (35) is the Trouton ratio χ_0/η . For a Newtonian fluid this is 3, but as noted above it is often much higher in polymer solutions. Furthermore, it was found by Minoshima et al.⁴⁰

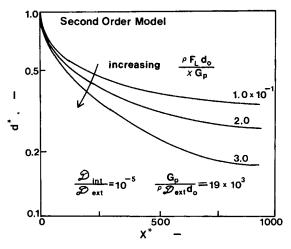


Fig. 5. Theoretical prediction of drawdown $d^*(d/d_0)$ as a function of distance from the spinneret $x^*(d/d_0)$ for the second-order model. We show the influence of increasing $\rho F_L d_0 / \chi_0 G_p$ at fixed $G_p / \rho \mathcal{D}_{ext} d_0$ of 19,000 and $\mathcal{D}_{int} / \mathcal{D}_{ext} = 10^{-5}$.

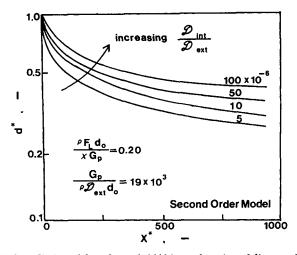


Fig. 6. Theoretical prediction of drawdown $d^*(d/d_0)$ as a function of distance from the spinneret $x^*(x/d_0)$ for the second-order model. We show the influence of increasing $\mathcal{D}_{int}/\mathcal{D}_{ext}$ at fixed $\rho F_L d_0/\chi_0 G_p$ of 0.20 and $G_p/\rho \mathcal{D}_{ext} d_0$ of 19,000.

in our laboratories that the spinline viscosity exceeds that found in normal elongational flow experiments. In Figure 7 it is shown that the higher the apparent Trouton ratio, the less the drawdown of the filament to occur.

In Figure 8 we show the predicted concentration variations across the fiber cross section.

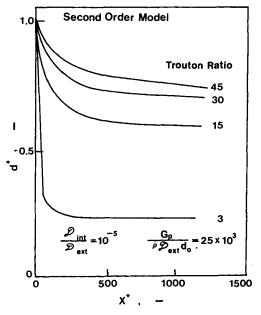


Fig. 7. Theoretical prediction of drawdown $d^*(d/d_0)$ as a function of distance from the spinneret $x^*(x/d_0)$ for the second-order model. We show the influence of increasing Trouton ratio $\chi_0/3\eta_0$ at fixed $G_p/\rho \mathcal{D}_{ext}d_0$ of 25,000 and $\mathcal{D}_{int}/\mathcal{D}_{ext}$ of 10^{-5} . The value of $\rho F_L d_0/\chi_0 G_p$ varies with values 0.30, 0.20, 0.10, and 0.02.

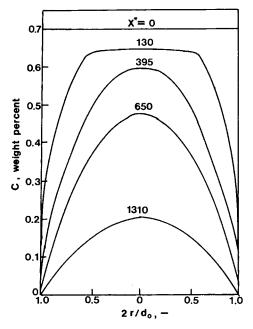


Fig. 8. Concentration profile across filament showing c as a function of r/(d/2) for varying x^* with $\rho F_L d_0/G_p = 0.20$, $G_p/\rho \mathcal{D}_{ext} d_0$ of 25,000 and $\mathcal{D}_{int}/\mathcal{D}_{ext}$ of 10^{-5} .

EXPERIMENTAL

Materials

Fibers were wet spun from solutions of nylon-66 (Du Pont Zytel) in formic acid (Fisher Scientific). The coagulation baths were water and 15 weight percent solutions of formic acid in water (compare our earlier papers^{19,20}).

Apparatus

The wet spinning apparatus was the same as that used in the authors earlier studies¹⁹ and described in more detail elsewhere.⁴¹ The spinneret diameter was 0.0381 cm and the extrusion rate 0.6 cm³/min.

Results and Comparison to Experiment

The nylon solutions emerging from the spinneret showed a swell d/D of 1.5. With the water coagulant, the value of d/D or d^* for the final fiber was 1.05 and 0.85 for the formic acid-water coagulant.

The pertinent dimensionless groups have values for this system of

$$\rho F d_0 / \chi G_p = 0.20$$

$$G_p / \rho d_0 \mathcal{D}_{\text{ext}} = 20,000, \quad (k_{\text{ext}})_0 d_0 / \mathcal{D} = 12.2$$

$$\mathcal{D}_{\text{int}} / \mathcal{D}_{\text{ext}} = 10^{-5}$$

A Trouton ratio (χ_0/η) of 30 was used.

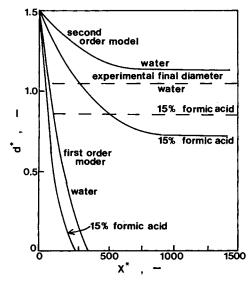


Fig. 9. Comparison of first-order and second-order models with experiment for spinning of nylon solution using water and 0.15 wt % formic acid coagulating baths.

In Figure 9, we contrast the predicted drawdown profiles and the observed final diameters for the filaments. There is rather good agreement between theory and experiment for the second-order model. The first-order model predicts a much too rapid drawdown.

We would like to thank Professor J. E. Spruiell for his helpful comments throughout the course of this study.

References

- 1. J. W. Swan, British Patent 5978 (1883).
- 2. H. de Chardonnet, United States Patent 394559 (1888).
- 3. H. de Chardonnet, United States Patent 531158 (1894).
- 4. C. H. Stearn, British Patent 1020 (1898).
- 5. W. C. Brinegar and M. E. Epstein, Appl. Polym. Symp., 6, 99 (1967).
- 6. C. D. Han and L. Segal, J. Appl. Polym. Sci., 14, 2973 (1970).
- 7. C. D. Han and L. Segal, J. Appl. Polym. Sci., 14, 2999 (1970)
- 8. J. Yerushalmi and R. Shinnar, IEC Proc. Res. Dev., 10, 196 (1971).
- 9. A. Ziabicki, Fundamentals of Fibre Formation, Wiley, New York, 1976.
- 10. G. R. McKay, J. Ferguson, and N. E. Hudson, J. Non-Newt. Fluid Mech., 4, 89 (1978).
- 11. J. J. Hermans, J. Colloid Sci., 2, 387 (1947).
- 12. P. H. Hermans and D. Vermaas, J. Polym. Sci., 1, 149 (1946).
- 13. A. Takizawa, Sen-I-Gakkaishi, 16, 842 (1960).
- 14. A. Takizawa, Sen-I-Gakkaishi, 17, 36 (1961).
- 15. R. M. Griffith, IEC Fundam., 3, 245 (1964).
- 16. D. R. Paul, J. Appl. Polym. Sci., 12, 383 (1968).
- 17. J. R. Booth, Appl. Polym. Symp., 6, 89 (1965).
- 18. M. E. Epstein and A. J. Rosenthal, Textile Res. J., 36, 813 (1976).
- 19. T. A. Hancock, J. L. White, and J. E. Spruiell, Polym. Eng. Sci., 20, 1126 (1980).
- 20. T. A. Hancock, J. E. Spruiell, and J. L. White, J. Appl. Polym. Sci., 21, 1227 (1977).
- 21. S. Y. Fok and R. G. Griskey, Appl. Sci. Res., 16, 191 (1966).
- 22. S. Y. Fok and R. G. Griskey, J. Appl. Polym. Sci., 11, 2417 (1967).
- 23. Y. Ohzawa, Y. Nagano, and T. Matsuo, J. Appl. Polym. Sci., 13, 257 (1969).

24. Y. Ohzawa and Y. Nagano, J. Appl. Polym. Sci., 14, 1879 (1970).

25. Y. Ohzawa, Y. Nagano, and T. Matsuo, Proc. 5th Int. Rheol. Cong., 4, 393 (1970).

26. I. Brezinsky, A. G. Williams, and H. L. LaNieve, Polym. Eng. Sci., 15, 834 (1975).

27. L. Prandtl and O. E. Tietgens, Fundamentals of Hydro and Aeromechanics, translated by

L. Rosenhead, Engineering Societies Monograph, New York, 1934.

28. Y. Sano and K. Orii, Sen-I-Gakkaishi, 24, 212 (1968).

29. I. Hamana, M. Matsui, and S. Kato, Meilland Textilber, 4, 382 (1969); 5, 499 (1969).

30. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.

31. T. K. Sherwood, R. L. Pigford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York, 1975.

32. S. Kase and T. Matsuo, J. Polym. Sci. A, 3, 2541 (1965).

33. S. Kase and T. Matsuo, J. Appl. Polym. Sci., 11, 251 (1967).

34. M. F. Johnson, N. N. Evans, I. Jordan, and J. D. Ferry, J. Colloid Sci., 7, 498 (1952).

35. Y. Ide and J. L. White, J. Appl. Polym. Sci., 18, 2997 (1974).

36. D. Harwood, H. Aoki, Y. D. Lee, J. F. Fellers, and J. L. White, J. Appl. Polym. Sci., 23, 2155 (1979).

37. H. Aoki, J. L. White, and J. F. Fellers, J. Appl. Polym. Sci., 23, 2293 (1979).

38. J. Crank, The Mathematics of Diffusion, Clarendon, Oxford, 1956.

39. J. C. Giddings, Dynamics of Chromatography, Vol. 1, Dekker, New York, 1965.

40. W. Minoshima, J. L. White, and J. E. Spruiell, J. Appl. Polym. Sci., 25, 287 (1980).

41. T. A. Hancock, Ph.D. Dissertation, University of Tennessee, Knoxville, TN, 1981.

Received August 29, 1980 Accepted March 13, 1981