Simulation of Kinetics and Heat and Mass Transfer for the Spinning of Chemical Fibers from Polymer Solutions

A. L. Kalabin and E. A. Pakshver

Tver State Technical University, Tver, Russia

All-Russian Research Institute of Synthetic Fiber, Moscow, Russia

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Abstract-A mathematical model for the kinetics of nonisothermal wet spinning of chemical fibers from polymer solutions is proposed. The model gives a way to calculate the kinetics of spinning and gelation simultaneously, using the phase diagram with regard to heat and mass transfer, layered two-phase patterns, and movable interfaces. The process is calculated numerically, and a comparison is made between calculated and experimental data.

In wet spinning of chemical fibers from polymer solutions, jets of a polymer solution pass through a spinning bath containing an agent that coagulates the polymer. The coagulant finds its way into the solution jets and accumulates there. When enough of the coagulant has been accumulated, the polymer solution is separated into a solid (gel-like) and a liquid phase. The gel-like phase is the primary structure of the fiber and controls its properties in many respects. The new polymer phase (gel) is a very viscous fluid. Its shear viscosity is high compared with the viscosity of the solution.

Although separate features of wet spinning of chemical fibers from polymer solutions are thoroughly discussed in [1 -3], a general quantitative theory of this process has not been created as yet. Some technological and physical problems for this process are studied in [4-7]. Papers [7-10] deal with calculating the flow of polymer-solution jets. Numerous attempts to create a model for wet spinning were made in [1-10]. However, the well-known models failed to take into account many important factors involved in the spinning process: all forces acting on the filament, the kinetics of phase separation in the jet, phase-equilibrium diagrams for the polymer-solvent-coagulant system, changes of rheological properties in the jet upon gelation, and others.

The gelation model proposed in [11] includes many important factors such as the phase-equilibrium diagram for the polymer-solvent-coagulant system to be formed, heat transfer, the temperature dependence of diffusion processes, the existence of a layered two-phase structure in spinning from polymer solutions, and a variable filament size in the process. However, that model fails to take into account the spinning kinetics.

The purpose of this paper is to create a kinetic model for the initial step of wet fiber formation (spinning) from a polymer solution with regard to the kinetics of phase separation.

Figure 1 illustrates the pattern of wet spinning from a polymer solution. The pattern includes five conventional zones: (I) flow of the solution through the spinneret channel; (II) expansion of the jet leaving the spinneret (Barrus effect); (II-III) phase separation, which begins when the solution leaves the spinneret and ends when the gelation across the jet is completed; (III-IV) filament extension; (V) filament collection. In each zone, the flow of the solution and filament is governed by its own mechanism. The first two zones are adequately described in the model proposed in [10]. This paper deals mainly with the third and fourth zones of the process.

The mathematical model to be developed in this paper is based on the following assumptions about fiber formation:
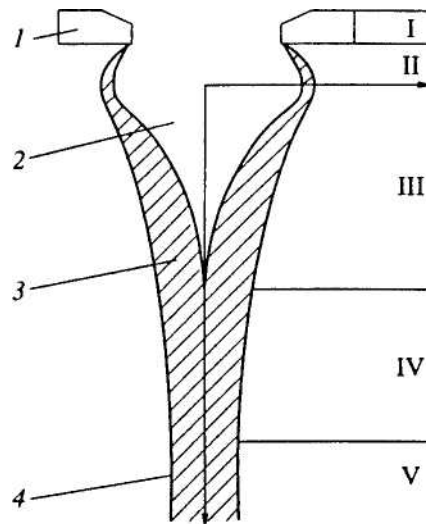

Fig. 1. Schematic diagram of wet spinning from polymer solutions: (I-V) conventional zones, (1) spinneret, (2) solution, (3) gel, and (4) fiber (filament).

(1) The problem is axially symmetric and one-dimensional. The coagulant diffuses solely in the radial direction and there is no convection. The fiber is an unbounded cylinder whose radius is small compared with the size of the spinning bath. Basic assumptions about gelation are the same as in [11].

(2) The contributions of gravity and surface tension to the motion of the jet of a polymer solution are neglected.

(3) The equation governing the motion of the filament is one-dimensional and the axial velocity is uniformly distributed over the jet cross section. Basic assumptions for the theory of thin-jet motion are the same as in [3].

(4) The solution and gel velocities are the same.

(5) The change in the jet radius due to the Barrus effect, shrinkage upon gelation, and mass transfer between the jet and spinning (coagulating) bath are ignored.

(6) The reference point in describing the process ($x = 0$) corresponds to the maximum radius of expanded jet after the latter has left the spinneret.

(7) The solution in the coagulating bath is stagnant.

(8) The process of fiber formation is considered for a single jet in the coagulating bath (interaction between jets is ignored).

(9) The solution and gel deformation in the jet is treated in terms of the Newtonian-liquid flow.

To describe the time-independent extension of the jet of a polymer solution in phase separation, we will consider a balance of forces acting on the moving jet. With the above assumptions and those given in [3], this balance can be written as

$$F_{rh}(x) = F_{rh}(0) + F_{in}(x) + F_{gd}(x). \tag{1}$$

The rheological force depends on the elastoviscous properties of the material (polymer solution or gel) and on the conditions of its deformation [3-7]. Assuming the additivity of the rheological forces of both polymer phases, we obtain

$$F_{rh}(x) = p_s S_s + p_g S_g, \tag{2}$$

$$F_{gd}(x) = 2\pi \int_0^x p_{xs} R_0 dx \tag{3}$$

$$F_{in} = G(v - v_0). \tag{4}$$

The fourth assumption transforms the time-independent continuity equation $G = \rho v S$ to

$$G = v(\rho_s S_s + \rho_g S_g), \tag{5}$$

where $p_s = \mu_s v'$, $p_g = \mu_g v'$, and $v' = dv/dx$ (here and below, the prime stands for differentiation with respect to x).

Let $R_0(x)$ be the current outer radius of the jet and $R = R(x)$ be the coordinate of the gelation front, which varies from R_o to $r = 0$ over the formation path. The current gel thickness $R_g(x)$ will be defined as the difference between the filament radius and gelation-front coordinate: $R_g(x) = R_0(x) - R(x)$. The areas of the phases are given by

$$S_s = \pi R^2, \quad S_g = \pi (R_0{}^2 - R^2). \tag{6}$$

Differentiating relation (1) with respect to x and substituting expressions (2)-(6) gives an equation that governs the motion of the jet:

$$\pi(\mu_g\delta/\mathrm{v}+\varphi R^2)\mathrm{v}''+\pi[\mu_g\delta(\mu'_g/\mu_g-\mathrm{v}'/\mathrm{v})/\mathrm{v}+R(2\varphi R'+R\varphi)-G/\pi]\mathrm{v}'-$$

$$-A_{gd}[\delta/\mathrm{v}+(1-k)R^2]^{0.5(1-\xi)}\mathrm{v}^{(2-\xi)}=0. \tag{7}$$

To solve equation (7), two boundary conditions were used. The initial velocity at $x = 0$ was determined from the continuity equation. The value of the velocity gradient at $x = 0$ was chosen numerically so that the final filament velocity v_{fin} would be equal to the experimental value of this quantity in the process to be simulated.

For the above problem to be closed, it is necessary to consider diffusion and heat transfer in the solution jet and, using the assumption that the phases in the system are in equilibrium, to determine the kinetics of phase separation, namely, the function $R_g(x)$. According to [II], the heat and mass transfer equations can be written as

$$\mathrm{v}\frac{\partial C_i}{\partial x} = \frac{1}{r}\frac{\partial}{\partial r}\left(D_i(T)r\frac{\partial C_i}{\partial r}\right), \tag{8}$$

$$\mathrm{v}\frac{\partial T_i}{\partial x} = \frac{1}{r}\frac{\partial}{\partial r}\left(a_i(T)r\frac{\partial T_i}{\partial r}\right)+q_i(r,t), \tag{9}$$

where $q_g(r, t) = 0$ and $q_s(r, t) = q_v.(r, t)$.

The initial conditions at $x = 0$ are

$$T_s(r, 0) = T_{init}(r), \tag{10}$$

$$C_s(r, 0) = C_{init}(r). \tag{11}$$

We use the following boundary conditions: at $r = R_o$ (the outer filament surface),

$$-\lambda_g(T)\frac{\partial T_g(R_0,x)}{\partial r} = \alpha[T_g(R_0,x)-T_0(x)], \tag{12}$$

$$C_g(R_0,0) = C_o(x); \tag{13}$$

at $r = R$ (the polymer-solution-gel interface),

$$C_s(R,x) = C_g(R,x), \tag{14}$$

$$D(T)\frac{\partial C_s(R,x)}{\partial r} = D_g(T)\frac{\partial C_g(R,x)}{\partial r}, \tag{15}$$

$$T_s(R,x) = T_g(R,x), \tag{16}$$

$$\lambda(T)\frac{\partial T_s(R,x)}{\partial r} = \lambda_g(T)\frac{\partial T_g(R,x)}{\partial r}; \tag{17}$$

at $r = 0$ (the filament center, symmetry conditions),

$$\frac{\partial T_g(0,x)}{\partial r} = 0, \quad \frac{\partial C_g(0,x)}{\partial r} = 0,$$

$$\frac{\partial T_s(0,x)}{\partial r} = 0, \quad \frac{\partial C_s(0,x)}{\partial r} = 0, \tag{18}$$

The heat source in (2) accounts for the heat liberated upon mixing the coagulant and solvent [9]. The source power is expressed as

$$q_v = \frac{q_m v}{H}\frac{\partial C}{\partial x}, \tag{19}$$

To determine the coordinate of the gelation front $R(x)$, it is necessary to use the phase-separation diagram for the ternary polymer-solvent-coagulant system. This diagram establishes the conditions for phase separation and influences the structure of fibers and their physicomechanical properties in wet spinning.

The gel thickness has to be determined by solving the transcendental equation

$$C[R(x),x] = C_{cr}[T(r, x)], \tag{20}$$

where the values of C_{cr} are taken from the phase diagram. This equation is solved for $R = R(x)$, the coordinate of the gelation front.

The system of equations (7)-(20) is a mathematical model for the uniaxial extension of a nonisothermal jet. The variation of temperature along the jet influences its longitudinal viscosity and, according to (7), its velocity. At the same time, the jet velocity influences the temperature profile because of being involved in equation (9) and through the heat-transfer coefficient in (12). Therefore, the system of equations (7)-(20) is closed. Its solution allows us to find the distribution over the formation path not only for the velocity and stress, but also for the radius, jet temperature, and gel thickness.

The presence of the movable boundary brings about additional difficulties in solving the problem. One way to pass from the movable to a stationary boundary is to use the von Mises transformation [12], in which a new dimensionless variable η is introduced:

$$\eta = r/R_0(x). \tag{21}$$

The system of equations (7)-(20) was solved using the implicit finite-difference method [12,13]. The algebraic system of equations was linearized by the method of iterations [13]. In the calculation, we used no more than three iteration steps. The method of iterations was used because the function $R_0(x)$ is not known in advance and the value of the radius has to be determined in the course of the solution. Nonlinear ordinary differential equation (7) in the system of equations (7)-(20) was solved by a fourth-order Runge-Kutta method with a constant step. The error in calculation did not exceed 1.5% for the chosen parameters of the numerical scheme.

Since the numerical method used in solving the problem fails to determine $C_0(r, x)$ analytically, gelation in the model given by (7)-(20) was calculated by the following method. When the system of heat and mass transfer equations was solved numerically, the distributions of the coagulant concentration $C(r, x_j)$ and filament temperature $T(r, x_j)$ over the filament radius were compared (at each step x_j in the coordinate x) with the phase diagram constructed in the same coordinates T and C. In doing so, we determined the polymer-solution filament fraction of radius $R(x)$ and the remaining gel-like filament fraction of thickness $R_g(x)$.

To estimate the effectiveness of the above mathematical model and its adequacy, calculated results were compared with experimental data [10, 14]. In [14], the kinetics of formation of oxalon fibers in the poly (n-phe-nylene-l,3,4-oxadiazole) (POD)-sulfuric acid-water system was studied. The dependence of the velocity $v(x)$ and filament radius $R_0(x)$ on the formation-path length x was measured for various values of the spinneret radius, polymer-solution flow rate, and coagulant concentration in the spinning bath.

For numerical simulation, we used the following values of formation parameters, which correspond to the experimental conditions reported in [14]: the spinneret channel radius $R_0(0) = 7.5 \cdot 10^{-5}$ m; the volume flow rate of the spinning solution $g=3.2 \cdot 10^{-10}$ m^3/s; the coagulant (water) concentration in the spinning bath $C_0 = 40$ mass %; the solvent (sulfuric acid) concentration, 60 mass %; the initial polymer concentration in solution $C_p = 5.3\%$ in 98% sulfuric acid; the sulfuric acid density $\rho_1 = 1840$ kg/m^3; the POD density $\rho_2 = 1430$ kg/m^3; the polymer-solution density was determined from the equation $\rho_s = 0.053\rho_2 + 0.947\rho_1$; the polymer-gel density was determined from the equation $\rho_g = 0.053\rho_2 + 0.947\rho_3$, where the 30% sulfuric acid density $\rho_3 = 1615$ kg/m^3; the density of the medium was defined as the density of 40% sulfuric acid, $\rho_0 = 1505$ kg/m^3 [15]; and the final filament velocity $v_{fin} = 0.05$ m/s. The kinematic viscosity of the medium was $v_0 = 1.3 \cdot 10^{-5}$ m^2/s [15]. According to [10], the
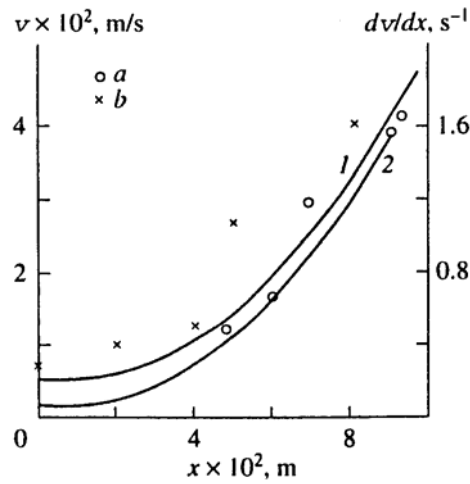
Fig. 2. Dependence of (1) the filament velocity v and (2) the velocity gradient v′ on *x:*
line, results calculated from the model; point, data [14]; (a) v values measured by the
velocity sensor; (b) v values calculated from changes in fiber diameter.

coagulant diffusivity in the solution was $D_s = 6 \cdot 10^{-10}\ m^2/s$. According to [3], the diffusivity in the polymer gel was $D_g = D_s/3$. The values of the model coefficients not given in this paper are borrowed from [11].

The kinetics of gelation was calculated using the phase diagram for the POD-sulfuric acid-water system [10]. For the experimental conditions of interest, the critical coagulant (water) concentration in the filament at which the gelation (coagulation) of the polymer system occurs is 30 mass %. For simulation, the initial value of the radius according to the sixth assumption and [14] was taken to be $R_0(0) = 0.125\ mm$. This value was used to calculate the initial velocity from continuity equation (5). The rheological parameters for the formation of fibers from the POD solution of interest are given in [10], where $\mu_s = 200\text{-}320\ Pa\ s$. For calculation, we took an average value of $\mu_s = 260\ Pa\ s$. The polymer-gel viscosity according to experimental data [2] was taken to be $\mu_g=6\mu_s$. As the difference between the solution and gel viscosities is large, we have to consider the rheological force in either polymer phase [equation (2)]. Since the experiment reported in [14] was conducted under isothermal conditions, heat transfer can be ignored.

The fiber formation in the POD-sulfuric acid-water system was chosen for numerical simulation because the experimental data for this system are quite complete.

Figures 2-4 illustrate calculated data and their comparison with experimental data. For comparison, we took the most important parameters of fiber formation accounting for its structure and properties (macromolecule orientation, macrodispersion, and crystallite sizes), as well as the most important process parameters (gelation time, tension, geometrical sizes at given temperatures and concentrations of polymer solution and coagulant) [2, 3]. Figure 2 illustrates the dependence of the filament velocity *v(x)* and

velocity gradient $v'(x)$ on the distance from the spinneret x in the spinning bath.

We calculated the dependence of the filament radius R_o and the gel-layer thickness R_g on the formation-path length x. The calculated results are plotted in Fig. 3. The S-shaped curve $R_g(x)$ is explained by the different dependence of R_x on x for the intervals $x < 0.04$ m and $x > 0.04$ m [II]. Complete (over the whole filament thickness) gelation occurs at $x \approx 0.067$ m, corresponding to the motion time $t = 4.1$ s. The time of complete gelation calculated after [11] for an average filament
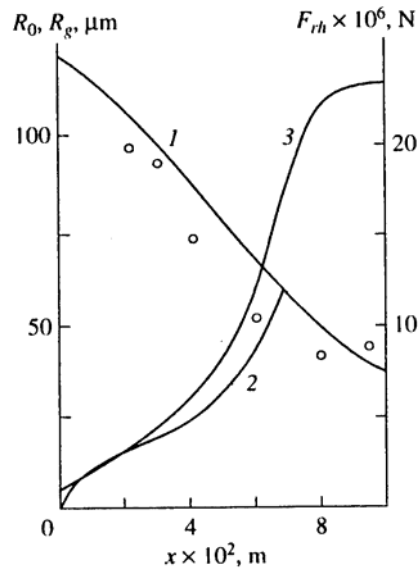
Fig. 3. Dependence of (1) the filament radius R_0, (2) gel-layer thickness R_g, and (3) the filament tension force F_{rh} on x: line, results calculated from the model; point, experimental data for $R_0(x)$ [14].
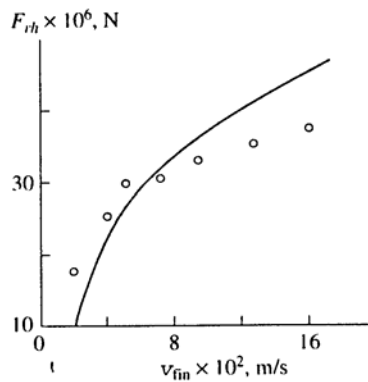
Fig. 4. Dependence of the filament tension force $F_{rh}(L)$ on the collection velocity v_{fin}: line, results calculated from the model; point, experimental data [14].

radius of $R \approx 9.2 \cdot 10^{-5}$ m is close to the above value: $t = 3.9$ s. Figure 3 illustrates the calculated curve of the filament tension force F_{rh} versus the formation-path length, which characterizes the stress distribution

in the filament. The filament stress is largely responsible for the orientation of molecules that provides the specified mechanical properties of the filament [3]. It should be noted that, after the complete gelation has been achieved, the force $F_{rh}(x)$ undergoes slight changes and the curve has a plateau. Figure 4 illustrates the calculated results for the dependence of the filament tension force $F_{rh}(L)$ [3] on the collection velocity v_{fin}.

The calculated results and their comparison with experimental data suggest that the model proposed in this paper satisfactorily describes the kinetics of wet spinning from polymer solutions. The discrepancy between the calculated and experimental data can be attributed both to the insufficient accuracy of the mathematical model, which was developed under certain assumptions, and to the error in the input data used in the calculations.

As distinguished from the well-known models [9, 10], the above model for the wet spinning of chemical fibers from polymer solutions gives a way to calculate the kinetics of spinning and gelation simultaneously, using the phase diagram with regard to heat and mass transfer, layered two-phase patterns, and movable interfaces.

NOTATION

$A_{gd} = a_c \rho_o (2/v_0)^{\xi}$ - constant;

a_c, a_n, γ, ξ - constants;

a_i - solution and gel thermal diffusivities, m^2/s;

C_0 - coagulant concentration in the bath solution, mass %;

C_{cr} - coagulant concentration at the instant of polymer phase transition at temperature T, mass %;

$C_{init}(r)$ - initial distribution of the coagulant concentration in the polymer solution, mass %;

$C(r, x)$ - coagulant concentration in the polymer-solution jet, mass %;

$C_f = a_c Re^{-\xi}$ - friction coefficient, $m^4/(kg\ s)$;

D - coagulant diffusivity, m^2/s;

$F_{gd}(x)$ - frictional force between the filament and medium, N;

F_{rh} - rheological force, N;

$F_{in}(x)$ - inertial force, N;

G - liquid mass velocity, kg/s;

g - volume flow rate, m^3/s;

H - specific heat capacity, J/(kg K);

$p_s\ p_g$ - solution and gel tension stresses, respectively, N/m^2;

$p_{xs} = 0.5c_jp_0^2\,v$ - shear stress, N/m^2;

q - specific power of the heat source, K/s;

q_m - specific heat of mixing per unit mass of coagulant, J/kg;

q_v - specific heat of mixing per unit volume of coagulant, K/s;

$R_0 = R_0(x)$ - jet (filament) radius varying from $R_0(0)$ to $R_0(L)$ over the formation path, m;

$R = R(x)$ - gelation-front coordinate varying from R_o to $r = 0$ over the formation path, m;

$R_g(x)$ - current gel thickness, m;

r - coordinate directed along the jet radius, m;

S - jet cross-sectional area, m^2;

S_s, S_g - solution and gel cross-sectional areas, respectively, m^2;

$T(r, t)$ - jet temperature at moment t at a point with coordinate r, K;

T_{init} - initial polymer-solution temperature, K;

T_0 - spinning-bath temperature, K;

v - filament velocity in the spinning bath, m/s;

$v_0 = v(0)$ - initial jet velocity, m/s;

$v(L) = v_{fin}$ - final velocity, m/s;

x - coordinate in the direction of the jet motion, m;

$\alpha = 2\lambda_o a_n Re^\gamma/R$ - heat-transfer coefficient, calculated from the relation $Nu = a_n Re^\gamma$, W/(m^2 K);

$\delta = G/(\pi p_g)$ - constant, m^3/s;

η - dimensionless variable defined by formula (21);

$k = \rho_s/\rho_g$ - constant;

λ - thermal conductivity, W/(m K);

μ - longitudinal viscosity of the solution and gel, Pa s;

v_0 - kinematic viscosity of the medium, m^2/s;

ρ_0 - medium density, kg/m^3;

ρ - liquid density, kg/m^3;

$\varphi = (\mu_s - \mu_g K)$ - constant parameter, Pa s;

$Nu = a_n Re^\gamma$ - Nusselt number;

$Re = 2R_0 v/v_0$ - Reynolds number.

SUBSCRIPTS AND SUPERSCRIPTS

init-initial value;

cr-phase transition;

g-polymer gel;

s-polymer solution;

$i = g$ for $R_0 > r > R$;

$i = s$ for $0 < r < R$.

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