THERMOTROPIC GELATION IN WET SPINNING OF FIBRES FROM POLYMER SOLUTIONS

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A mathematical analytical model of thermotropic gelation in heat exchange of a jet of polymer solution in a spinning bath was plotted by considering the phase equilibrium diagram of the polymer-solvent-precipitator system and the heat transfer process. The law of the change in gel layer thickness in time was determined and the duration of total thermotropic gelation was estimated. It was shown that the qualitative behavior of the functions of the gel layer thickness versus time is close to a unit step function, the duration of total gelation for the thermotropic process is approximately 0.1 sec. and the corresponding value of the Fourier number. $Fo_g \sim 2$.

More than one-third of the chemical fibres manufactured in the world - cellulose, polyacrylonitrile, aramid, polyvinyl chloride, etc. - are now manufactured by wet spinning from polymer solutions. All of these technologies have a common mechanism of fibre formation. Beginning with S. P. Papkov's studies [1], the gelation process in spinning has been considered with respect to the phase state of the polymer solutions. The kinetics of fibre formation (gelation) was investigated experimentally in [2], and there are also studies on modeling this process [2-6] based on its diffusion nature.

The growth rate of the gel coating in time and the duration of total gelation in a small jet of spinning solution are very important features in wet spinning technology. Our previously proposed [7] model for describing gelation in "wet" spinning of chemical fibres from polymer solutions differs from the existing models [2-6] due to the possibility of calculating the gelation kinetics using the phase diagram.

The phase transition in polymer systems can be caused by not only a change in the composition of the solvent (addition of a precipitator) but also by a change in the temperature or application of a mechanical field. The kinetics of attaining the condition of phase equilibrium to a significant degree determines the structure and physicomechanical properties of the gel. The gel phase, in turn, is the primary structure of the fibre which greatly determines its properties. The further investigation of gelation from polymer solution is pressing. The formation of a gel in thermotropic

conditions [8], where fibre formation takes place due to heat exchange alone without diffusion, is described in recent publications on gelation.

Thermotropic gelation is examined in the present study.

The current gel layer thickness can be determined from the transcendental equation in [7]

$$C[R(r),t]=C_{cr}[T(r,t)], \tag{1}$$

where $C[r,t]$ is the concentration of precipitator in the polymer solution jet (r is a coordinate along the radius of the jet; t is the time); C_{cr} is the concentration of precipitator at the time of the phase transition at temperature T; the value of C is found from the phase diagram of the polymer-solvent-precipitator system.

Equation (1) is solved relative to $R = R(t)$ - the coordinates of the gelation front. The current gel layer thickness R_g (t) is determined as the difference between the radius of the fibre R_0 and the coordinate of the gelation front $R_g(t) = R_0 - R(t)$. This relation and Eq. (1) can be used to find the gel layer thickness as a function of time $R_g(t)$.

The calculation of $R_g(t)$ for a nonlinear model of gelation is reported in [7]. An approximate linear model of the process, expressed in algebraic equations, will be examined for the analysis of the change in the size of the gelation zone in time $R_g(t)$ and for the estimations. It is hypothesized that the qualitative shape of $R_g(t)$ will be preserved when the nonlinear model is
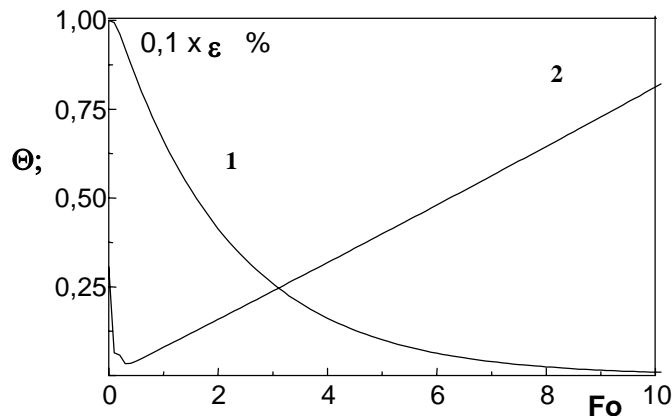

Fig. 1. Reduced fibre temperature θ(1) and relative error of calculation ξ(2) calculated with Eq. (4) for z = 0.5 vs. Fourier number.

simplified. This assumption is based on the fact that the nonlinearity, which allows calculating the gelation kinetics from the point of view of a heat-exchange process, only results in a quantitative change in the thermal diffusivity and heat exchange coefficient in time and space,

i.e., it makes it possible to consider the difference of these coefficients in solution and gel with a dynamic change in the gel film thickness.

We will make the following assumptions in the subsequent examination:

1) spinning is thermotropic, i.e., the initial concentration of precipitator in the polymer solution is equal to the concentration of precipitator in the spinning bath, so that $C[R,t]$ = const;

2) we will use one average value of the thermal diffusivity in the polymer solution and gel, and it is constant;

3) the fibre radius R_0 is constant;

4) heal exchange on the surface of the fibre corresponds to Newton's law, i.e., to boundary conditions of the third kind [2].

When these conditions are satisfied, the relation is simplified:

$$T[R,t]=T_{cr}=const \qquad (2)$$

where T_{cr} is the temperature of the system at the time of the phase transition for defined concentrations of precipitator and polymer.

On this basis, the model from [7] can be transformed into a linear heat equation for an unbounded cylinder. The dimensionless temperature distribution θ over the radius of the fibre as a function of dimensionless time Fo (Fourier number) is the known solution of the linear transfer problem [9] and is

$$\theta(z,Fo)=[T(r,t)-T_g]/(T_0-T_g)=\sum_{n=1}^{\infty} A_n J_0(\mu_n z)\exp(-\mu_n^2 Fo), \qquad (3)$$

where $z = r/R_0$; $Fo = at/R_0^2$; a is the thermal diffusivity; T_g is the ambient temperature; T_0 is the initial temperature of the solution; $A_n = 2Bi/[J_0(\mu_n)(\mu_n^2 + Bi^2)]$; J_0 is a zero-order Bessel function of the first kind; μ_n is the solution of the characteristic equation; $Bi = aR_0/\lambda$ is the Biot number; the dimensionless quantity θ_{cr} corresponds to T_{cr}; is the heat transfer coefficient; λ is the thermal conductivity coefficient.

Substituting Eq. (3) for the center of the cylinder with $r=0$ in Eq. (2), we obtain an equation whose solution is the gel layer thickness as a function of time $R_g(t)$. The gelation process can be considered complete when the temperature at a point the maximum distance from the surface of the fibre (its center) attains a value sufficient for the phase transition of the polymer solution into a gel, i.e., $T(0,t) = T_{cr}$ is satisfied.
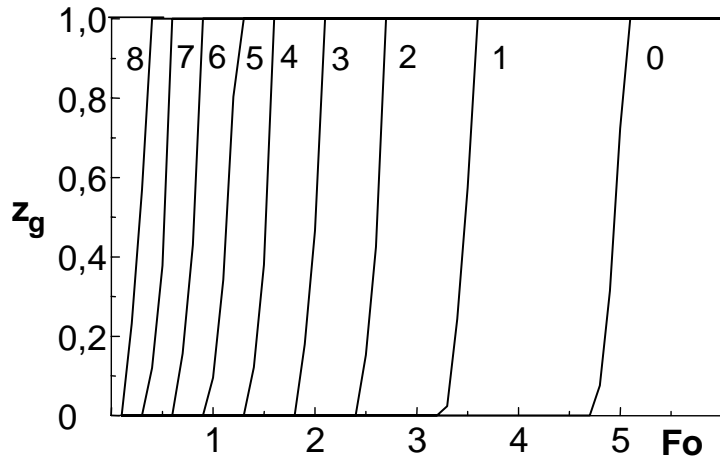
Fig. 2. Dimensionless gel thickness z_g vs. dimensionless time - Fourier number for different values of θ_{cr}: 0)0; 1)0.1;2)0.2;3)0.3;4) 0.4; 5)0.5; 6) 0.6; 7) 0.7; 8) 0.8.
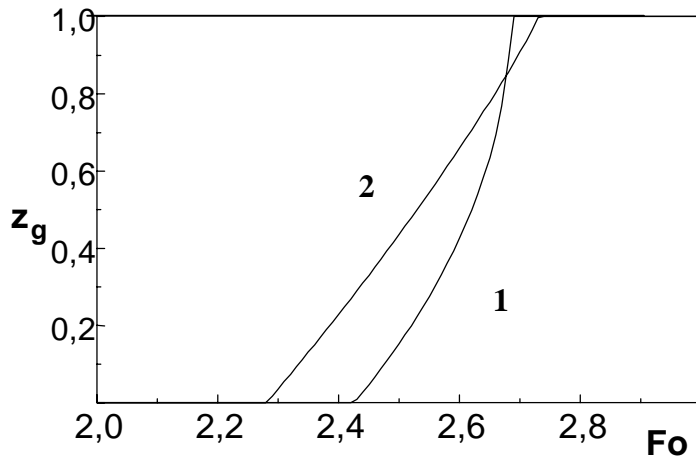
Fig. 3. Dimensionless gel thickness z_g vs. Fourier number for $\theta_{cr} = 0.2$. Curve 1 was obtained from the solution of Eq. (2); curve 2 was calculated with Eq. (5).

Use of the linear model does not qualitatively simplify Eq. (2) - it is still transcendental. We will use the existing method of analysis of solutions of a parabolic transfer equation from [10] based on use of an approximate solution for small and large times for the given process for transforming it into an algebraic equation. The following approximate solution for an infinite cylinder with boundary conditions of the third kind was obtained:

$$\theta(z,Fo)=[1-(z)^n]exp[-B(Fo-Fo_1)], \qquad (4)$$

where constants m, Fo_1, and n are determined from the equations

$$\frac{2}{Bi}m^2 + (2Bi + 4 - \mu_1^2)m + 4Bi - \mu_1^2(Bi+2) = 0,$$

$$Fo_1 = \frac{\ln A_1}{2(1+m/Bi)}\left(\frac{1}{Bi} + \frac{1}{m+2}\right),$$

$$Fo_1 = \frac{1}{2n(n+1)}\left[1 - \frac{4}{3(n+2)}\right].$$

The following quantities are then determined

$$A = (1+n/Bi)^{-1},$$

$$B = 2(1+m/Bi)[1/(m+2)+1/Bi]^{-1}.$$

This method of investigation assumes separation of the duration of the process into two parts. The value of the Fourier number Fo_1 corresponding to the lime the temperature in the center of the cylinder begins to change $r = 0$, i.e., at a point the maximum distance from the surface of the fibre, is the dividing point. In the first half-open interval, for $Fo < Fo_1$, use of the expression for the calculation which is accurate for a semi-infinite medium is proposed in [10]. Equation (4) is the refined value of the first term of infinite series (3). Quantities A_1 and μ_1 in the first term of this series are included in the system. The data
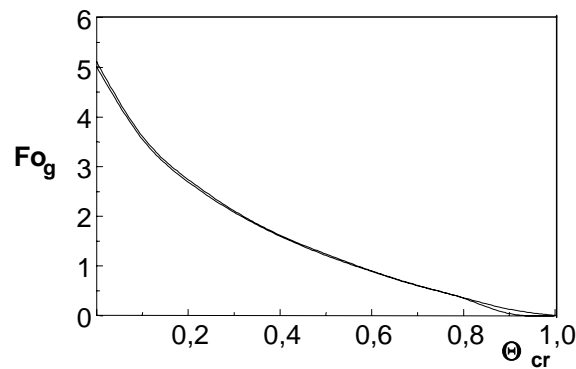

Fig. 4. Fourier number corresponding to total gelation Fo_g vs. dimensionless critical temperature θ_r .

from calculations with Eq. (4) were compared with the accurate data calculated with Eq. (3) to evaluate the adequacy of Eq. (4); the results are shown in Fig. 1. We obtain from Eq. (4) the expressions for the dimensionless polymer gel thickness $z_g = R_g(t)/R_0$ in explicit form as a function of time for a defined critical temperature

$$z_x=\{[1-\theta_{cr}exp(B(Fo-Fo_1))]\}^{1/n}.\tag{5}$$

We also obtain from Eq. (4) the equation for estimating the duration of total gelation in dimensionless form:

$$Fo_g=Fo_1+ln[(1-A)/\theta_{cr}]/B.\tag{6}$$

We will represent Eq. (6) as the sum

$$Fo_g=Fo_1+Fo_{cr},\tag{7}$$

where Fo_1 is the time required for the temperature in the center of the jet with $r = 0$ to change by approximately 1 % relative to the initial temperature; Fo_{cr} is the duration of the change in the temperature from the initial temperature to the temperature required for gelation for the given concentration.

This approach will allow distinguishing two stages in the gelation process - with duration Fo_1 and Fo_{cr}.

Equation (6), presented in dimensionless form, establishes the dependence of the duration of total gelation t_g on the process parameters of the temperature of the medium (spinning bath), initial temperature of the polymer solution, phase diagram of the system, fibre radius, and thermal diffusivity

$$t_g = R^2 \{F_{01} + ln[(1-A)(T_0-T_g)/(T_{cr} -T_g)]/ B\} / a.\tag{8}$$

Converting the description of thermotropic gelation to dimensionless form based on the theory of similarity due to establishment of internal links between the variables reduces the number of parameters. Instead of quantities $a, \lambda, \alpha, R, T_0, T_{cr}$, and T_c, the Biot number and reduced temperature θ_{cr} are used. The number of arguments in the functions is reduced from 7 to 2 in this way.

To test the serviceability of the proposed estimation of the duration of total gelation, numerical modeling was conducted with Eqs. (4)-(8). The spinning conditions were selected in the polyacrylonitrile (PAN)-dimethylformamide (DMF)-water system, for initial concentrations of the PAN-DMF-water solution of 20:78.4:1.6% and DMF-water spinning bath of 98:2% were selected. Consider the solution of Eq. (2) for these spinning conditions in this system for a concentration of water of $C = 2\%$ according to [11]. In these conditions, the spinning bath at normal temperature cannot coagulate the spinning solution, and only shifts the phase equilibrium curve (in temperature-concentration of polymer coordinates) to the region of higher temperatures. This system can form a gel while cooling. The following

values of the process parameters were used: $R_0 = 0.05$ mm, $T_0 = 50°C$; $T_g = -10°C$. The thermal conductivity coefficient and thermal diffusivity required for solving the heat problem for PAN-DMF solution were taken from [12] without consideration of their temperature dependence:

$\lambda = 0.2$ W/(mK), specific heat capacity $G = 2100$ J/(kgK) for a density of $\rho = 950$ kg/m³. We will hypothesize that the thermal diffusivity of the fibre, averaged for temperature and time, is equal to $a = \lambda/G\rho = 10^{-7}$ m²/sec. Due to the lack of data, the thermophysical properties of the gel were assumed to be the same as for the solution. The value of $\alpha = 10^3$ W/(m²K) was determined with the data in [2], then $Bi = 0.25$. In calculating the values for substitution in Eq. (4), we find that $n = 1.081$, $m = 9.86 \cdot 10^{-3}$; $Fo_1 = 0.126$.

The dimensionless thickness of the solidified polymer (gel) as a function of time $z_g(Fo)$ is shown in Fig. 2. It was obtained by solving Eq. (2) using Eq. (3). This curve has a shape close to a unit step function. The numerical estimation of the value of $t_g = 0.1$ was calculated for $\theta_{cr} = 0.155$ [11] for the PAN-DMF-water system.

To check Eq. (5), the calculated curves of the dimensionless gel thickness z_g as a function of time Fo are compared in Fig. 3. Curve 1 was obtained from Eqs. (2) and (3) and curve 2 was obtained with Eq. (5) for $\theta_{cr} = 0.2$. The following additional conditions were satisfied in the calculation: first, if $z_g > 1$ or $z_g < 0$, then $z_g = 0$; second, for $y = 1 - \theta_{cr} \exp[B(Fo - Fo_1)]$, if $y > 1$, then $z_g = 0$ and if $y < 0$, $z_g = 1$. These conditions are determined with the physical meaning of dimensionless gel thickness z_g, which is only established in the interval from 0 to 1. A comparison of curves I and 2 indicates the satisfactory performance of Eq. (5).

The calculations with Eq. (6) are shown in Fig. 4. The curve of the Fourier number Fo_g, whose values correspond to total gelation, as a function of the critical temperature θ_{cr}, determined from the phase diagram, was obtained. The curves obtained from the solution of Eqs. (2) and (3) and calculated with Eq. (5) are almost the same, which confirms their efficiency. Algebraic equation (5) allows calculating the increase in the gel thickness in time much more simply than by solving the transcendental system of Eqs. (2) and (3).

A comparison of the curves of the thickness of the solidified polymer as a function of time obtained for isothermal [13] and thermotropic fibre formation showed that they have a very different qualitative shape.

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