

## **ESTIMATION OF THE TOTAL GELATION TIME IN WET SPINNING OF CHEMICAL FIBRES FROM SOLUTIONS OF POLYMERS**

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*An estimation of the total gelation time in "wet" spinning of chemical fibres from solutions of polymers was proposed based on the model of gelation in [2], which uses a phase diagram. The equations for this estimation were analyzed with the results of numerical modeling and the workability of the method was tested with experimental data.*

More than one-third of all chemical fibres manufactured in the world (viscose, polyacrylonitrile, aramid, polyvinyl chloride) are spun from solutions of polymers by the "wet" method. A common mechanism of fibre formation unites the technologies for manufacture of all of these fibres.

Gelation is one of the most important processes in the technology for manufacture of chemical fibres from polymer solutions. Gelation is a complex process which greatly determines the subsequent behavior and quality of the fibre and is difficult to predict. This process is most frequently considered from qualitative positions - in assessing the structure and properties of a fibre gel. Beginning with the research by S. P. Papkov [1], gelation during spinning has much more rarely been considered from the positions of the phase state of the polymer solutions. This approach allowed qualitatively characterizing both the kinetics of formation of the fibre and its properties. The kinetics of fibre formation (gelation) have been investigated in many experimental studies [2], and there are also studies on modeling of this process [2-6] based on its diffusion nature.

Growth of the polymer shell (gel) in time is an important moment in the technology for wet spinning of chemical fibres. A model is proposed in [7] for describing gelation in wet spinning of chemical fibres from solutions of polymers which differs from the existing models [2-6] due to the possibility of calculating the kinetics of gelation with the phase diagram, taking into consideration heat and mass transfer from the mobile phase boundary. This model is a system of nonlinear differential equations in partial derivatives which must be solved with the appropriate computer and software. The total gelation time during which gelation takes place over the entire thickness of the jet is the basic parameter of fibre formation in wet spinning. This quantity can be used to estimate the minimum fibre path length in the spinning bath in spinning of fibres of different linear density.

A method is proposed here for estimating the total gelation time ( $t_g$ ) and establishing the

dependence of  $t_g$  on such parameters of the technological process as the concentration of precipitator in the bath and polymer solution, the phase diagram of the system, the fibre radius, the diffusion coefficient, and the temperature.

The running thickness of the gel can be determined from the transcendental equation

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

where  $C(R, t)$  is the concentration of precipitator in the polymer solution;  $C_{cr}$  is the concentration of precipitator at the time of the phase transition at temperature  $T$ , determined from the phase diagram of the polymer-solvent-precipitator system.

This equation is solved relative to  $R = R(t)$  - the coordinates of the gelation front. Then we determine the running thickness of the gel  $R_g(t)$  as the difference between the fibre radius  $R_0$  and the coordinate of the gelation front  $R_g(t) = R_0 - R(t)$ . This relation and Eq. (1) can be used to determine the thickness of the gel layer as a function of time  $R_g(t)$ .

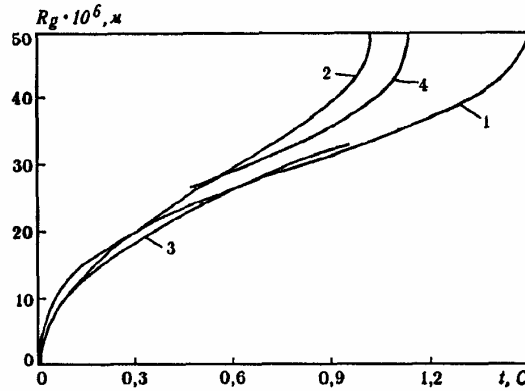


Fig. 1. Gel thickness vs. duration of gelation: 1) with Eq. (1) from [7]; 2) with Eq. (2) for the linear model; 3) with Eq. (5); 4) with Eq. (6).

$R_g(t)$  is calculated in [7] for a nonlinear model of gelation. An approximate linear model of the gelation process, expressed in algebraic equations, is examined below for analyzing the change in  $R_g(t)$  and estimating  $t_g$ . It is hypothesized that the qualitative shape of  $R_g(t)$  is preserved in simplification of the nonlinear model. This assumption is based on the fact that the nonlinearity, which allows calculating the kinetics of gelation, with respect to the diffusion process only results in a quantitative change in the diffusion coefficient in time and space, i.e., it allows calculating the diffusion coefficients in solution and gel for a dynamic change in the thickness of the gel film.

Let us make the following assumptions: the initial temperature of the polymer solution and the temperature of the spinning bath are equal (isothermal spinning); for this reason, the

temperature of the fibre remains constant:  $T(r, t) = const$ ; one value of the averaged diffusion coefficient of the precipitator in the polymer solution and gel is used; the diffusion coefficient of the precipitator is constant, and the model from [7] is transformed into a linear diffusion equation for an unbounded cylinder. When these conditions are satisfied, Eq. (1) is simplified:

$$C [R, t] = C_{cr} = const. \quad (2)$$

A similar approach is proposed in [6] for a linear diffusion equation.

The total gelation time can be determined with the linear model using the tabulated solution of the linear problem in [8] for the center of a cylinder ( $r = 0$ ). Actually, we can consider the gelation process to be complete when the concentration of precipitator at a point maximally distant from the surface of the fibre - the center of the fibre - attains values sufficient for the phase transition of the polymer into a gel, i.e., the relation  $C(0, t) = C_{cr}$  is satisfied.

Use of the linear model does not qualitatively simplify Eq. (2) - it remains transcendental. For this reason, we will use the method of analysis of solutions of a parabolic transfer equation in [9], based on the use of an approximate solution for brief and long times for the given transfer process, for transforming it into an algebraic equation. This method assumes separation of time  $t_g$  into two parts. The value of the Fourier number  $Fo_I = Dt_I/R_0^2 = 0.081$ , corresponding to the onset of a change in the concentration at the center of the cylinder ( $r = 0$ ), i.e., at a point maximally distant from the surface of the fibre - the source of the precipitator, where  $D$  is the diffusion coefficient, is the point of separation. It is proposed in [9] that an approximate expression for calculating the concentration which is accurate for a semi-infinite medium [8, 9] be used for the first half-open interval, for  $t < t_I$ .

$$C_p(r, t) = C_g + (C_n - C_g) \operatorname{erf} \{ [R_0 - R(t)] / 2\sqrt{(Dt)} \}, \quad (3)$$

where  $C_n$  is the initial concentration of precipitator in the polymer solution;  $C_g$  is the concentration of precipitator in the bath.

In the second half-open interval, for  $t > t_I$ , the approximate solution in [9] is

$$C_p(r, t) = C_g + (C_n - C_g) [1 - (r/R_0)^{1.5t}] \exp [-5.79 (Fo - Fo_I)]. \quad (4)$$

This relation is an accurate expression of the first term of an infinite series, which is the solution of the linear diffusion equation for an infinite cylinder with boundary conditions of the first kind [8, 9]. When substituted in Eq. (2), Eqs. (3) and (4) allow obtaining the expression for the thickness of gelation of the polymer in explicit form as a function of time for a certain critical

concentration  $C_{cr}$ . It follows from Eq. (3):

$$R_g(t) = \sqrt[3]{(Dt/[erf^{-1}\{\theta\}])} \quad (5)$$

$$\text{for } 0 < t < t_1$$

where  $erf^{-1}$  is an inverse function of  $erf$ ;  $\theta = (C_{cr} - C_g)/(C_n - C_g)$ . We obtain from Eq. (4):

$$R_g(t) = R_o \{1 - [1 - \{\theta\} \exp [5.79 (Fo - Fo_1)]]\} \quad (6)$$

$$\text{for } t_g > t > t_1$$

An equation for estimating the gelation time is proposed in [2, 3, 6, 10]:

$$t_g = f(C_g, C_0) R_o^2 / D. \quad (7)$$

The results of the analysis can be used to determine function  $f$  from Eq. (6) as

$$f(C_g, C_0, C_{cr}) = Fo \quad (8)$$

$$\text{for } Fo > Fo_1$$

It follows from Eqs. (7) and (8) that:

$$t_g = R_o^2 [Fo_1 - \ln(\theta) / 5.79] / D. \quad (9)$$

Since  $\theta$  varies within the limits of 1 to 0, it is obvious that  $\ln(\theta) \leq 0$ . For this reason, Eq. (9) can be represented as the sum

$$t_g = t_0 + t_{cr} \quad (10)$$

where  $t_0$  is the time required for the concentration of precipitator in the center of the jet ( $r = 0$ ) to vary by approximately 1 % relative to the initial concentration (the stream of precipitator attains the point maximally distant from the surface of the fibre - its center);  $t_{cr}$  is the duration of the change in the concentration of precipitator from the initial concentration to the concentration required for gelation ( $C_{cr}$ ) at the given temperature.

Such an approach allows separating two stages of duration  $t_0$  and  $t_{cr}$ , respectively, in the gelation process.

Equation (10) establishes the dependence of  $t_g$  on the parameters of the technological process, namely: the concentration of precipitator in the bath and in the polymer solution, the phase diagram of the system, the fibre radius, and the diffusion coefficient.

Numerical modeling and a calculation with the experimental data were conducted with Eqs. (7) and (8) to verify the workability of the proposed estimation of the total gelation time:

$R_0 \cdot 10^5, m$	$t_g, sec$		
	Calculation with the model in [2]	Data from [8]	Estimation with Eq. [9]
7	3	2,8	3
10,5	6,8	6,4	6,7
15	13,8	12,5	13,6

"Soft" spinning conditions in the polyacrylonitrile (PAN)-dimethylformamide (DMF)-water system for initial concentrations of PAN + DMF solution of 20 + 80 wt. % and DMF + water spinning bath of 80 + 20% were selected for numerical modeling. Consider the solution of Eqs. (1) and (2) for "soft" spinning conditions in this system, where the concentration corresponding to gelation of the polymer at the given temperature is equal to  $C_{cr} = 2\%$  based on the phase diagram of the PAN-DMF-water system [11]. We will assume that the diffusion coefficient of the precipitator to the fibre, averaged for temperature and time, is equal to  $D = 2.08 \cdot 10^{-10} m^2/sec$ , and  $R_0 = 0.05 mm$ .

The curve of the thickness of the hardened polymer (gel) as a function of time  $R_g(t)$  is S-shaped (Fig. 1). It shows that at the beginning of the process,  $R_g$  is proportional to  $\sqrt{t}$ , then the curve becomes almost linear, and  $R_g$  is proportional to a higher degree of time with a further increase in the duration of gelation. The calculations in Fig. 1 with Eqs. (5) and (6) are in good agreement with the results of the solution of the nonlinear problem for  $t < t_l$  and are in satisfactory agreement for  $t > t_l$ . The solution of Eq. (2) for the time interval  $[0, t_{gl}]$  (curve 2) is compared with the solution obtained with the model of gelation in [7] (curve 1). The curves of the thickness of the hardened polymer as a function of time, obtained with the results of modeling and in solving diffusion equation (1), have the same qualitative shape.

For the given system, the total gelation time determined with the tabulated solution of the linear problem for the center of a cylinder ( $r = 0$ ) [8] is equal to  $t_{gl} = 1.03 sec$ . A comparison of this estimation with the value of  $t_g = 1.5 sec$  calculated in [7] shows that it is understated by one third. This is because the linear model does not allow considering the change in the diffusion coefficient in gelation, while it is indicated in [2] that the diffusion coefficient in the gel is several times smaller than in the polymer solution. For  $D$ , the value of  $Fo_l$  corresponds to  $t_l = 0.97 sec$ , when the concentration in the center of the fibre attains 1%, which is in agreement with the assumptions made.

The results of numerical modeling confirm the workability of the proposed method of

estimating the total gelation time. To verify this method, the results of the calculation and the experimental data from [12], in which spinning of PAN fibre from a water-thiocyanate solution of the polymer was investigated, were compared. The results of measuring  $R_g(t)$  in spinning of fibres with different radii are reported in this study. The experiment was conducted with the following spinning parameters: monofilament radius of  $R_0 = 0.15, 0.105, 0.07 \text{ mm}$ ; isothermal conditions - the initial temperature was equal to the temperature of the precipitator in the bath,  $T_n = T_s = 11^{\circ}\text{C}$ ; concentration of precipitator (water) in the bath,  $C_g = 90\%$ , initial concentration (water) in the polymer solution,  $C_0 = 42.68\%$ .

The diffusion coefficients for the precipitator into the polymer solution required for the calculations were determined with the experimental data in [12]. For a fibre radius of  $R = 0.105 \text{ mm}$ ,  $D = 2.2 \cdot 10^{-10} \text{ m}^2/\text{sec}$ . This value ensures agreement of the experimental and calculated total gelation time of  $t_g = 6.8 \text{ sec}$ . The value of  $t_g$  for fibres with different radii  $R_0$  based on the model from [2] and Eq. (9) was then calculated with this value of  $D$ . The results reported in the table above are in very satisfactory agreement. For comparison,  $t_g$  was determined based on the tabulated solution of the linear problem for the center of a cylinder ( $r = 0$ ) in [8].

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