ESTIMATION OF THE PARAMETERS OF MECHANOTROPIC GELATION IN WET SPINNING OF FIBRES

A. L. Kalabin* and E. A. Pakshver**

A mathematical analytical model of stretching of a jet of polymer solution was constructed. Estimations of the total mechanotropic gelation time, longitudinal rate, and rate gradient were obtained. It was shown that the order of the total gelation time for such a process in the system considered is within the limits of 1-10 sec.

The existence of phase transitions is one problem in the physical chemistry of polymer materials. Specific aspects of phase transitions in polymer systems are most completely presented in [1-3]. In our opinion, the applied aspect of phase equilibrium in gelation in solution of macromolecules in "wet" spinning of chemical fibres is important.

The reaction of the components in a solution and phase transitions into a gel are a function of a series of factors - concentration, temperature, external pressure, mechanical stress, composition of the solvent, pH, electric field [4, 5]. The kinetics of attaining the state 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 solutions is pressing.

We will define gelation as the phase transition of a polymer from liquid phase to gel when the external conditions change. This transition can be represented as the movement of a point reflecting the state of the system in multidimensional space whose axes are the quantities indicated above. This movement takes place from an initial point to the surface (in the plane-curve) of liquid-gel phase equilibrium of the polymer to which the phase diagram of the system corresponds. In this case, the external parameters correspond to the transition point, and their values are considered transitional.

We know that a gel can be formed under the effect of a mechanical field [4-7]. However,

the use of this effect explicitly is not known in industrial practice of processing isotropic solutions. It hypothetically takes place in spinning of systems capable of forming liquid-crystalline solutions [8]. The experiments we conducted with concentrated solutions of polyacrylonitrile in dimethylformamide cross-linked with cobalt and nickel salts showed that solidification of such a solution is possible under the effect of mechanical (tensile) force. A gel fibre is formed, coated with droplets of solvent separated from it as a result of syneresis.

The goal of the present study was to create an analytical model of stretching of the polymer solution jet to obtain estimations of the parameters of mechanotropic gelation in wet spinning of chemical fibres.

In elaborating the mathematical model, the following assumptions were made about the gelation process:

- the equation of movement of the jet is unidimensional, obtained in the assumption that the distribution of the axial velocity over the cross section of the jet is homogeneous; the basic assumptions in the theory of motion of a thin jet are given in [2];

- for movement of the polymer solution jet, the contribution of gravity and the surface tension force can be neglected;

- the initial point of description of the process $x = 0$ corresponds to the maximum radius of the jet in its expansion after coming out of the channel; the Barus effect is not considered in the examination.
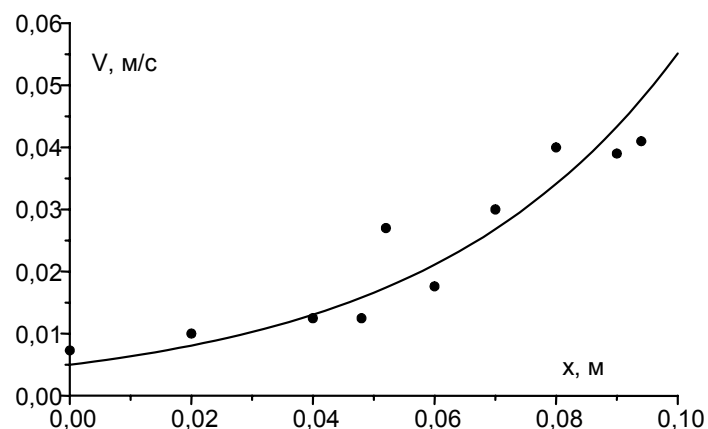

Fig. 1. Jet velocity $v(x)$ vs. x. Curve; calculation with the model; points: experimental data in [9].

The current gel thickness can be determined from the transcendental equation [9]

$$C[R(r),t] = C_{ch}[T(r,t), v'(r,t)], \tag{1}$$

where $C[R(r),t]$ is the concentration of precipitator in the polymer solution jet; C_{ch} ; is the concentration of precipitator at the time of the phase transition at temperature T and longitudinal velocity gradient v' ; the value of C_{ch} is determined from the three-dimensional phase diagram of the polymer-solvent-precipitator system; r is a coordinate directed along the radius of the jet; r is the time.

This equation is solved relative to $R = R(t)$, the coordinates of the gelation front.

In examining thermotropic spinning [10], Eq. (1) is transformed, becoming

$$T[R,t] = T_{ch} = const, \tag{2}$$

where T_{ch} , is the temperature of the system at the time of the phase transition for constant values of the concentrations of precipitator and polymer and the longitudinal velocity gradient.

By analogy, we can hypothesize that in examining mechanotropic spinning, Eq. (1) is transformed into an equation of the form

$$v' [R,t] = v'_{ch} = const, \tag{3}$$

where v'_{ch} is the longitudinal velocity gradient of the solution at the time of the phase transition for a defined concentration and temperature of precipitator and polymer.

For describing the mechanical field that arises in steady-state stretching of the polymer solution jet in phase separation in it, we will use the well-known approach based on the balance of forces acting on the jet; according to [2] and the assumptions used, it is

$$F_{rh}(x) = F_{rh}(0) + F_{in}(x) + F_{gd}(x), \tag{4}$$

where the forces are $F_{ch}(x)$ - rheological, $F_{in}(x)$ - inertial, $F_{gd}(x)$ - hydrodynamic friction force between jet and medium; x is the coordinate in the direction of movement.

Our previously proposed [9] system of equations allows simultaneously calculating both the kinematics and dynamics of movement of the jet with consideration of the rheological properties of each phase and phase separation with consideration of the biphasic laminar structure and mobility of the phase boundaries. For studying mechanotropic gelation, we will use the assumption concerning the constancy of the tensile stress of the fibre

$$F_{rh} (x) = F = const. \tag{5}$$

It is shown in [9,11] that the quantity $F_{rh}(x)$ varies within the range of 0 to 40 μN before

gelation begins so that we will define $F = \text{const}$ as the average value in this range:

$$F = S_{Pxx} = \eta Sv'(x),$$ (6)

Where $P_{xx} = \eta v'(x)$ is the expansion stress of the solution; $S = \pi R^2$ is the area of the section of the jet; $G = Spv$ is the steady-state continuity equation, or $g = Sv$; g is the mass and volume consumption of solution; p is the density of the polymer solution; η is the longitudinal dynamic viscosity.

We obtain the ordinary differential equation

$$\frac{1}{v}\frac{dv}{dx} = \frac{F\rho}{G\mu}$$ (7)

whose solution, considering initial condition $v_0 = v(0)$, is

$$v(x) = v_o exp(\beta x)$$ (8)

for

$$\beta = F\rho/(G\eta) = F/(g\eta)$$ (9)

Then the relation for the longitudinal velocity gradient becomes

$$v'(x) = v_0 \beta exp(\beta x)$$ (10)

The complete gelation time t_m is a fundamental parameter of the gelation process in wet spinning. This is the time after which the gelation process has taken place over the entire radius to the center of the jet. Using this quantity, the length of the fibre path in the spinning bath can be estimated in spinning fibres of different linear density at different speeds.

For estimating t_m, we obtain a relation from determining the velocity $v = dx/dt$, from which it follows that $t(x) = \int dx/v(x)$, or substituting Eq. (8):

$$t_m(x_0) = \int_0^{x_0} \frac{dx}{v(x)} = \frac{1}{\beta v_0} - \frac{1}{v_0} = [1-exp(-\beta x_o)]/\beta v_0$$ (11)

where x_0 is the value of the coordinate corresponding to the value of v' at which a phase transition is possible with the other parameters in the system being fixed.

The values of the parameters from [11, 12], in which spinning of poly-(p-phenylene-l,3,4-oxadiazole) (POD) fibres into aqueous solution of sulfuric acid was examined, were used for

numerical modeling with the proposed model. The experiment was conducted with the following values of the quantities [11]: volume flow rate of spinning solution of $g= 3.2*10^{-10}$ m^3/sec; initial longitudinal velocity of $v_0 = 5*10^{-3}$ m/sec; $p_1= 1840$ kg/m^3 is the density of sulfuric acid; $p_2= 1430$ kg/m^3 is the density of POD; p_3 is the density of the polymer solution, calculated from the relation $p_s =0.053p_2 + 0.947p_1 = 1820$ kg/m^3. The rheological characteristics for the examined case of spinning fibres from POD solution are reported in [12]. The value of $\eta = 320$ Pa*sec was used in the calculations. We will define the average value of $F_{rh}(x)$ from [11] as $F = 20$ μ N.

The calculated and experimental data of the jet velocity $v(x)$ as a function of x are shown in Fig. 1 for comparison.

We give the following numerical estimations for verifying the validity of the proposed calculation of the total gelation time based on Eqs. (8)-(11). We obtain the value of coefficient $\beta_{calc} = 24$ m^{-1} from calculated Eq. (9). For comparison with the experimental data, from Eq. (10) we obtain

$$\beta \ exp = ln[v(x_0)/v_0]/x_0 \ , \tag{12}$$

which, for $x_0 = 0.08$ m and corresponding $v(x_0) = 0.04$ m/sec, gives the experimental value of $\beta \ exp =26$ m^{-1}. The difference is less than 8%.

We obtain the estimation of $t_m(x_0)$ with Eq. (11) for $v(x_0) = 0.04$ m/sec and $v'(x_0) =1.7$ sec^{-1}, equal to $t_m =7.8$ sec. The tensile stress is then

$$P_{xx}(x_0)=\eta \ v'(x_0) \approx \ 544 \ Pa \tag{13}$$

The analysis of Eq. (11) shows that the maximum value of the total gelation time as $x_0 -> \infty$ will be:

$$t_m=\frac{1}{\beta v_0} = 8.3 \ sec. \tag{14}$$

It follows from the same expression that the approximate value of coordinate x_0 for the case examined can be determined from the condition $exp(-\beta \ x_0) = 0$, which is satisfied for $\beta x_0 \approx 3$ with an error of less than 5%. Then

$$x_o=3/\beta = 0.12m. \tag{15}$$

In view of the assumptions on the gelation process used in this article, X_0 can be estimated

from Eq. (10), i.e., the value of the coordinate corresponding to *v'* at which a phase transition is possible in the system:

$$x_0 = ln[v'(x_0)/\beta \, v_0]/\beta \qquad (16)$$

It follows from the assumption concerning the homogeneous distribution of the axial velocity over the cross section of the jet that the curve of the thickness of the solidified polymer as a function of time will have qualitatively the same shape for thermotropic and mechanotropic gelation.

REFERENCES

1. S. P. Papkov, *Phase Equilibrium in the Polymer-Solvent System* [in Russian], Khimiya, Moscow (1981).
2. A. Ziabicki, *Fundamentals of Fibre Formation,* Wiley, New York (1976).
3. A. E. Nesterov and Yu. S. Lipatov, *The Phase State of Polymer Solutions and Blends* [in Russian], Naukova Dumka, Kiev (1987).
4. G. M. Bartenev and S. Ya. Frenkel', *Polymer Physics* [in Russian], Khimiya, Leningrad (1990).
5. S. A. Vshivkov and E. V. Rusinova, *Vysokomolek. Soedin.,* B40**,** No. 6, 1051-1061 (1998).
6. A. Ya. Malkin and S. G. Kulichikhin, *Vysokomolek. Soedin.,* B38**,** No. 2, 362-374 (1996).
7. S. Ya. Frenkel' and G. K. El'yashevich, in: *Theoiy of Chemical Fibre Spinning* [in Russian], Khimiya, Moscow (1975), p. 91.
8. N. A. Plate (ed.), *Liquid-Crystal Polymers* [in Russian], Khimiya, Moscow (1988).
9. A. L. Kalabin and E. A. Pakshver, *Teor. Osn. Khim. Tekhnol,* 31, No. 6, 574-579 (1997).
10. A. L. Kalabin and E. A. Pakshver, *Khim. Volokna,* No. 4, 38-41 (2000).
11. V. V. Romanov, N. P. Kruchinin, and A. S. Semenova, *Khim. Volokna,* No. 1, 25 (1984).
12. T. M. Getmanyuk and A. L. Yarin, *Inzh.-Fiz. Zh.,* 55, No. 1, 50-59 (1988).