

MATHEMATICAL MODELING OF POLYMER MELT CRYSTALLIZATION  
WITH THE PHASE TRANSITION VELOCITY TAKEN INTO ACCOUNT

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A model is proposed for melt crystallization taking account of the heat transfer and phase transition rates. The adequacy of the model is shown by experimental data.

It is assumed in the mathematical description of the melt crystallization processes of low-molecular-weight compounds that the phase transition proceeds at high velocity [1-3]. For polymer systems [4-6] a noticeable phase transition velocity is observed during supercooling the melt 10-50° relative to the equilibrium melting point  $T_m$ , while the characteristic phase transition time is  $10^1$ - $10^5$  sec. The characteristic heat transfer time  $R^2/a_a$  with the governing dimension of the crystallization domain,  $R = 10^{-3}$ - $10^{-1}$  m, say, is on the order of  $10^1$ - $10^5$  sec. Therefore, the crystallization rate can be delimited by both the phase transition velocity (kinetic domain) and the heat transfer velocity (the thermal domain is the formation of the mobile phase transition boundary) or by both simultaneously (mixed domain). The thermal domain case is ordinarily associated with the Stefan problem [1-3].

Let us perform a phenomenological analysis. We introduce the degree of completeness of the phase transition ( $0 \leq \theta \leq 1$ ), which we shall consider as a local quantity by giving it the field  $\theta(r, \tau)$ . Such an approach can be considered legitimate since the characteristic dimension of the crystalline formations is  $10^{-6}$  m [4, 7] while the dimension of the crystallization domain is  $10^{-3}$ - $10^{-1}$  and the function  $\theta$  can be considered continuous in space. In this situation, the equations of the kinetics of the phase transition and the heat transfer should be solved jointly with the appropriate boundary and initial conditions.

Taking account of the liberation of the heat of phase transition the heat transfer differential equation can be written in the form

$$\rho \frac{\partial(cT)}{\partial\tau} = \text{div}(\lambda\nabla T) + \rho\Delta h_k \frac{\partial\theta}{\partial\tau}. \quad (1)$$

The change in the thermophysical characteristics during the phase transition must be taken into account in this equation. Let us use the two-phase model [6]

$$\begin{aligned} \rho(\theta) &= \rho_a(1 - \theta) + \rho_k\theta = \rho_a(1 + \delta_\rho\theta); \\ c(\theta) &= c_a(1 + \delta_c\theta); \quad \lambda(\theta) = \lambda_a(1 + \delta_\lambda\theta), \end{aligned} \quad (2)$$

where  $\delta_\rho = (\rho_k - \rho_a)/\rho_a$ ;  $\delta_c = (c_k - c_a)/c_a$ ;  $\delta_\lambda = (\lambda_k - \lambda_a)/\lambda_a$ , and we give the linear dependence of the heat of the phase transition on the temperature [5]

$$\Delta h_k = \Delta h_m T / T_m. \quad (3)$$

Taking (2) and (3) into account, (1) can be transformed into

$$\frac{\partial T}{\partial\tau} = a_a\Phi_1(\theta)\nabla^2 T + a_a\Phi_2(\theta)(\nabla\theta \cdot \nabla T) + T\Phi_3(\theta)\frac{\partial\theta}{\partial\tau}, \quad (4)$$

where

$$\Phi_1(\theta) = \frac{1 + \delta_\lambda\theta}{(1 + \delta_\rho\theta)(1 + \delta_c\theta)};$$

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$$\Phi_2(\Theta) = \frac{\delta_\lambda}{(1 + \delta_\rho \Theta)(1 + \delta_c \Theta)}; \Phi_3(\Theta) = \frac{\Delta h_m / T_m C_a - \delta_c}{1 + \delta_c \Theta}.$$

We describe the kinetics of the phase transition by the following integral equation [4, 8]

$$\Theta(r, \tau) = \begin{cases} 0 & \text{for } \tau \leq \tau_m, \\ 1 - \exp \left\{ -n \int_{\tau_m}^{\tau} K_n \left[ T(r, t), \frac{\partial T(r, t)}{\partial t} \right] (\tau - t)^{n-1} dt \right\} & \text{for } \tau > \tau_m. \end{cases} \quad (5)$$

For a nonisothermal phase transition process the constant  $K_n$  can be represented in the form

$$K_n \left( T, \frac{\partial T}{\partial t} \right) = K(T) \left[ 1 - \frac{\tau^* T_m^p}{T(T_m - T)^p} \frac{\partial T}{\partial t} \right], \quad (6)$$

where

$$K(T) = K_0 \exp \left[ -\frac{BT_m^s}{T(T_m - T)^s} \right] \quad (7)$$

is a constant of the phase transition velocity under isothermal conditions. The dependence of  $K_n$  on the rate of change of the temperature is explained by the diminution of the critical dimensions of the crystalline seed as the temperature diminishes, which is associated with the additional rate of stable seed formation.

For the one-dimensional case and the symmetric problem of heat transfer with boundary conditions of the third kind [2], we represent the mathematical description of the crystallization process by the following system of integrodifferential equations by introducing the dimensionless coordinate  $X = r/R$  and the time  $Fo = a_a \tau / R^2$ :

$$\frac{\partial T}{\partial Fo} = \Phi_1(\Theta) \left( \frac{\partial^2 T}{\partial X^2} + \frac{\Gamma}{X} \frac{\partial T}{\partial X} \right) + \Phi_2(\Theta) \frac{\partial \Theta}{\partial X} \frac{\partial T}{\partial X} + T \Phi_3(\Theta) \frac{\partial \Theta}{\partial \tau}; \quad (8)$$

$$\Theta(X, Fo) = \begin{cases} 0 & \text{for } Fo \leq Fo_m, \\ 1 - \exp \left[ -n (K^*)^n \int_{Fo_m}^{Fo} \Phi \left( T, \frac{\partial T}{\partial Fo_t} \right) (Fo - Fo_t)^{n-1} dFo_t \right] & \text{for } Fo > Fo_m; \end{cases} \quad (9)$$

$$\Phi \left( T, \frac{\partial T}{\partial Fo_t} \right) = \varphi(Fo_t) \left[ 1 - \frac{Fo^* T_m^p}{T(T_m - T)^p} \frac{\partial T}{\partial Fo_t} \right]; \quad (10)$$

$$\varphi(Fo_t) = \exp \left[ -\frac{BT_m^s}{T(T_m - T)^s} \right]; \quad (11)$$

$$T(1, Fo) - T_c = -\frac{1 + \delta_\lambda \Theta(1, Fo)}{Bi} \frac{\partial T(1, Fo)}{\partial X}; \quad (12)$$

$$\frac{\partial T(0, Fo)}{\partial X} = 0; \quad T(X, 0) = T_0(X), \quad (13)$$

where  $Fo_t = a_a t / R^2$ ;  $Fo^* = a_a \tau^* / R^2$ ;  $Fo_m = a_a \tau_m / R^2$ ;  $Bi = \alpha R / \lambda_a$ ;

$$K^* = \frac{R^2}{a_a} K_0^{1/n}; \quad (14)$$

$$T(X, Fo_m) = T_m. \quad (15)$$

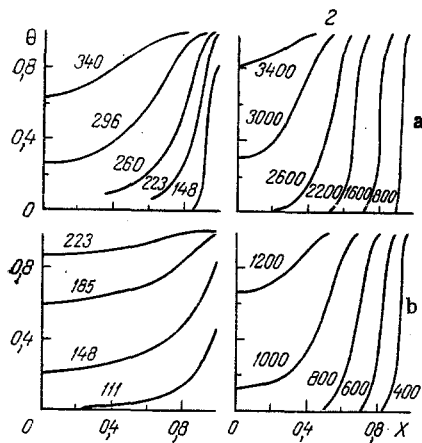


Fig. 1

Fig. 1. Design profiles of the degree of completeness: a) plate, b) sphere; 1)  $R = 0.004$  m ( $K^* = 4.0$ ); 2)  $R = 0.016$  m ( $K^* = 64.0$ ). Numbers on the curves are the time in sec.

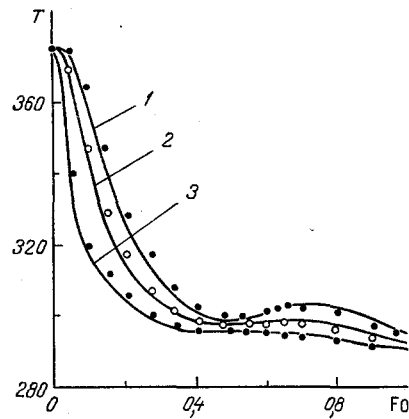


Fig. 2

Fig. 2. Comparison of the computed (curves) and experimental (points) values of the temperature for crystallization of a urethane polyester: 1) along the cylinder axis; 2) at a distance of 0.008 m from the axis; 3) 0.012 m from the axis.

The criterion  $K^*$  is the ratio between the characteristic heat transfer time  $R^2/a_a$  and the characteristic time of the phase transition process  $K_0^{-1}/\rho$ . The extreme cases  $K^* \rightarrow \infty$  and  $K^* \rightarrow 0$  will correspond to the progress of crystallization in the thermal and kinetic domains, respectively. If the temperature of the cooling medium is a given function of time, then the system of equations (8)-(13) is closed and can be solved numerically. Otherwise, it is necessary to have still another equation for  $T_c$ . For instance, let us consider the case for which the polymer melt in the form of spherical granules, a cylindrical bar, or sheet and a cooling medium move in the displacement mode. The medium is heated here because of cooling of the polymer. Analogously to what was done in [9], an ordinary differential equation can be obtained for  $T_c(\tau)$  and written in the dimensionless variables

$$\frac{dT_c}{dFo} = - \frac{1 + \delta_\lambda \Theta(1, Fo)}{\gamma} \frac{\partial T(1, Fo)}{\partial X};$$

$$T_c(0) = T_{c,i},$$

where

$$\gamma = \pm \frac{G_c c_c}{(1 + \Gamma) G_\tau c_a}$$

(the plus sign corresponds to direct flow motion of the polymer and the cooling medium, and the minus to the opposite).

A finite-difference method is used for the numerical solution of the system (8)-(13). In principle, the derivatives  $\partial\theta/\partial Fo$  and  $\partial\theta/\partial X$  in (8) can be evaluated analytically by applying the rule of differentiating an integral with respect to a parameter to the relationship (9). However such a means of solution is awkward enough. Consequently, a difference approximation of the derivative of both the temperature and of the degree of completeness is introduced, where the time derivative of  $\theta$  is evaluated in one step  $h_{Fo}$  with a lag as compared to the time derivative of the temperature. For the relationship  $h_{Fo}/h_x^2 < 0.3$  of the time step and the coordinate step the numerical solution of (8)-(13) is stable.

Cooling of the melt at a given point to the melting temperature  $T_m$  precedes the phase transition process and the analysis is performed up to this time  $Fo_m$  without using the kinetic equations (9)-(11). Starting with the time value  $Fo_m(X)$  determined from the condition (15) for different coordinates during the integration, the kinetic equations are introduced into the computation.

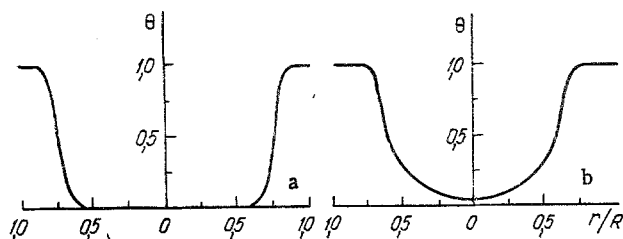


Fig. 3. Visually observable urethane polyester crystallization process in a cylinder and the corresponding theoretical profiles of the completeness of the phase transition [ a)  $\tau = 720$ , b)  $1020$  sec].

Computations for the crystallization of urethane polyester of molecular mass 25,000 are represented in this paper. The following values of the parameters  $n = 3.5$ ;  $s = 2$ ;  $p = 3$ ;  $B = 10.1$  K;  $K_0 = 1.6 \cdot 10^{-5} \text{ sec}^{-3.5}$ ,  $\tau^* = 114$  sec;  $T_m = 316$  K have been obtained as a result of investigating kinetics of the phase transition in isothermal [10] and nonisothermal conditions. The thermal diffusivity coefficients were determined for the amorphous and crystalline phases by the methods of the regular regime [2], and they are  $a_a = 0.88 \cdot 10^{-7}$  and  $a_k = 0.78 \cdot 10^{-7} \text{ m}^2/\text{sec}$ . By using the method of integral heat balance in application to the polymer cooling and crystallization process in a cylinder with heat insulated endfaces, we estimate the parameters  $\delta_\lambda = -0.06$ ;  $\delta_\rho = 0.05$ ;  $\delta_c = 0.01$ ;  $\Delta h_m/c_a = 38$  K.

Variants of urethane polyester crystallization computations are presented in Fig. 1. For  $R = 0.016$  m ( $K^* = 64.0$ ), the crystallization process is characterized by a strongly inhomogeneous profile of  $\theta$  and it is possible to speak of a certain provisional phase transition front. For  $R = 0.004$  m ( $K^* = 4.0$ ) the  $\theta$  profile is more homogeneous. As computations show, for  $K^* < 0.1$  it is possible to speak about the homogeneous progress of the crystallization process in space (kinetic domain), while for  $K^* > 10$  the formation of a mobile phase separation "boundary" (thermal domain) is observed. Computed and experimental dependences of the temperature on the Fourier number are represented in Fig. 2 for crystallization of a urethane polyester melt in a cylinder of radius 0.016 m with heat insulated endfaces. The temperature of the cooling water was  $T_c = 289$ , and the initial melt temperature was  $T_0 = 375^\circ\text{K}$ . Good agreement is observed between the theoretical and experimental data.

The theoretical  $\theta$  profile and the visually observable pattern of the crystallization process are compared in Fig. 3. The experiments were performed as follows. The cylinder of the polymer melt was placed in cooling, agitated water at the constant temperature  $T_c = 289^\circ\text{K}$  after having been in a thermostat at a  $T_0 = 393^\circ\text{K}$  temperature. After definite time intervals, transverse cuts were made on the cylinder and photographed. The distribution of the degree of phase transition completeness can be assessed qualitatively by the distribution of polymer transparency along the radius of the cut. A "blurred" phase transition front is observed up to considerable times for cylinders of radius 0.0115 (see Fig. 3) and 0.0075 m. The phase transition proceeds at all points of the polymer bulk in the concluding stage of the crystallization process. Analogous photographs and computations performed for cylinders of less than 0.002-0.003 m radius show that the provisional phase transition front is missing even in the initial stages while the crystallization process proceeds in the whole polymer mass.

In conclusion we note that the theoretical and experimental results obtained yield a foundation for considering the crystallization process within the framework of problems with mobile phase separation boundaries only in the limit case of  $K^* \rightarrow \infty$ . For  $K^* \rightarrow 0$  the concept of a phase transition front generally loses all physical meaning.

#### NOTATION

$R$ , radius of the cylinder or sphere or half the plate thickness;  $T_m$ , melting point;  $a$ , thermal diffusivity coefficient;  $\theta$ , degree of phase transition completeness;  $r$ , radius-vector;

$\tau$ ,  $t$ , running time and the time of crystalline seed formation;  $\rho$ , density;  $c$ , specific heat at constant pressure;  $\lambda$ , heat conduction coefficient;  $T$ ,  $T_0$ , melt running and initial temperatures;  $T_c$  and  $T_{c,i}$ , running and initial temperatures of the cooling medium;  $\Delta h_m$ , heat of fusion;  $K_n$ ,  $K$ , velocity constant for nonisothermal and isothermal phase transition processes;  $n$ ,  $K_0$ ,  $\tau^*$ ,  $B$ ,  $s$  are kinetic parameters;  $p = 2$ , a spherical seed;  $p = 3$ , cylindrical or rectangular seeds;  $\Gamma = 0$  (plate), 1 (cylinder), 2 (sphere);  $\tau_m$ , time to reach the melting point at a given point;  $G_c$ ,  $c_c$ , mass flow rate and the specific heat of the cooling agent;  $G_T$ , mass flow rate of the polymer melt;  $a$  and  $k$ , subscripts denoting the amorphous and crystalline phases of the polymer, respectively.

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