with n "nonoperating" caps; W_G, total fluidization number; ΔP_c, resistance of the cap, kPa; ΔP_c°, resistance of the cap at critical flow rate, kPa; ΔP_{sz}, resistance of the stagnant zone, kPa; ΔP_{sz}°, maximum resistance of the stagnant zone at the instant of its destruction, kPa; ξ, resistance coefficient of the cap; ρ_g, ρ_p, density of the gas and of the packed layer, respectively, kg/m³; ε, porosity of the bed.

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ALTERNATIVE METHOD OF DESCRIBING THE KINETICS OF CRYSTALLIZATION

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We present a comparative analysis of a macrokinetic type equation and the Avrami–Kolmogorov equation for describing the crystallization of polymers. We show that the macrokinetic equation agrees with experiment over the whole range of the degrees of transformations.

A standard method of describing the isothermal kinetics of crystallization based on the Avrami–Kolmogorov equation

$$\alpha(t) = 1 - \exp(-Kt^n) \tag{1}$$

has been available in the scientific literature for a long time. However, this equation is difficult to use to solve practical problems which are complicated by heat transfer, since there is no sufficiently simple generalization of Eq. (1) for a nonisothermal process. This forces us to turn to other methods of describing $\alpha(t)$ quantitatively. We solve this problem by employing the so-called macrokinetic approach, which is widely used to solve problems of

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chemical kinetics. Instead of formulating an equation for α, this method seeks an equation for the transformation rate α as a function of α, just as in chemical kinetics the transformation rate β is described by some function of the degree of transformation β. A macrokinetic equation was proposed in [1] to describe the isothermal crystallization of polymers

$$\dot{\eta}(t) = [A_1 + A_2 S_1(\eta)](\alpha_e - \eta) \tag{2}$$

or, by considering the relative ("reduced") degree of transformation $\alpha = \eta/\alpha_p$, an equation for $\dot{\alpha}$ (t) can be written in the form

$$\dot{\alpha}(t) = [A_1 + A_2 S(\alpha)](1 - \alpha), \tag{3}$$

analogous to the autocatalytic type equation of chemical kinetics. Physical reasons for an equation of this type were given in [1], and it was shown in [2] that such an equation can be applied to nonisothermal phase transition processes, and may even be preferred for a quantitative description of crystallization processes of a number of polymers. The question of the general agreement of the forms of the $\alpha(t)$ relations given by Eqs. (1) and (3) is still unclear, and this is important in view of the fact that Eq. (1) gives a good description of a large volume of experimental data. The present paper is devoted to a consideration of this question.

First of all we note that if the generality of the function $S(\alpha)$ is not restricted, Eq. (1) can be considered as a special case of (3). In differential form Eq. (1) has the form

$$\frac{1}{1-\alpha}\frac{d\alpha}{dt} = K^{1/n} n \left(\ln \frac{1}{1-\alpha}\right)^{\frac{n-1}{n}}. \tag{4}$$

Equation (3) can be written in a similar form:

$$\frac{1}{1-\alpha}\frac{d\alpha}{dt} = A_1 + A_2 S(\alpha). \tag{5}$$

It is clear that Eq. (4) can be obtained from (5) by setting

$$A_1 = 0,\ A_2 = K^{1/n} n,\ S(\alpha) = \left(\ln \frac{1}{1-\alpha}\right)^{\frac{n-1}{n}}.$$

It should also be noted that in Eq. (4) the initial rate of crystallization is assumed zero, whereas, in (5) $\dot{\alpha} = A_1$ as $\alpha \to 0$. This reflects the fact that nuclei of the new phase can generally be found, or are instantaneously and spontaneously formed in the melt, and this is not taken into account in the Avrami—Kolmogorov equation.

The special case of Eq. (3) when $S(\alpha) = D\alpha$, i.e., $S(\alpha)$ is a linear function, is of great interest. This form of the function $S(\alpha)$ was used successfully in [1, 2]. Let us consider for this case the relation between Eq. (1) and the integral macrokinetic equation, which can easily be obtained from Eq. (3):

$$\alpha(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)}, \tag{6}$$

where $C_0 = A_2'/A_1$; $C_1 = A_1 + A_2'$.

The possibility of replacing the nonlinear function $\omega(\alpha) = (\ln 1/(1-\alpha))^{(n-1)/n}$ by a linear function can be shown from graphs of $\omega(\alpha)$ for n = 2, 3, and 4 (Fig. 1). These curves are actually well described by the function $f(\alpha) = A_1 + A_2'\alpha$ over a wide range of values of α except for a finite region. This is not unexpected, since as $\alpha \to 1$ the right-hand side of Eq. (4) approaches ∞; in contrast with this, it follows from Eq. (5) for $S(\alpha) = D\alpha$ that $A_1 + A_2 D\alpha$ has a well-defined finite value, which also leads to the divergence mentioned above. It should be emphasized, however, that the experimental data on the isothermal crystallization of polymers in the final stage of the process generally lie somewhat below the theoretical curve calculated with Eq. (1) [3, 4]; i.e., in just this region Eq. (1) turns out

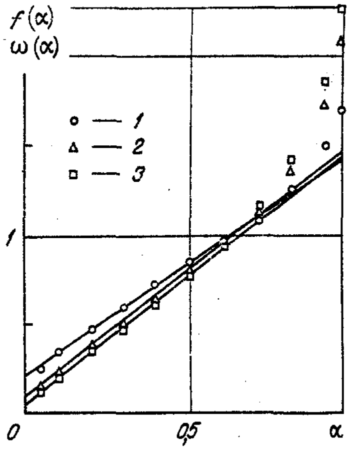

Fig. 1

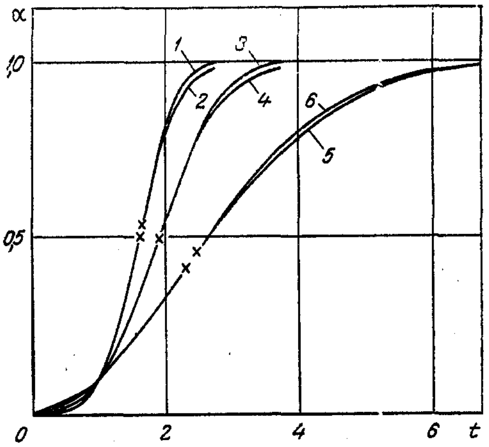

Fig. 2

Fig. 1. Comparison of macrokinetic (5) and Avrami—Kolmogorov (4) equations for various n ($K^{1/n}$ n = 1): points are ω(α): 1) n = 2; 2) 3; 3) 4; solid curves are f(α).

Fig. 2. Comparison of theoretical crystallization isotherms calculated from Eqs. (1) and (6): 1, 3, 5) from Eq. (1) for n = 4, 3, and 2 (K = 0.1 min^{-n}); 2, 4, 6) from (6) with values of C_0 and C_1 found from (12) and (13).

to be defective. This emphasizes the fact that Eq. (5), or its nonisothermal variant, is to be preferred in calculating the crystallization of polymers.

Let us estimate the divergences which may arise in the processing of experimental data according to Eqs. (1) and (6). This is most simply done by mathematical modeling. To do this it must be shown that it is always possible to find two pairs of constants K and n, C_1 and C_0, which when substituted into Eqs. (1) and (6) respectively give theoretical functions α(t) which are sufficiently close in the whole time interval. The divergences which can arise, as a rule, should not exceed the experimental errors. If we assume that

$$\exp(-Kt^n) \approx \frac{C_0+1}{C_0+\exp(C_1 t)}, \tag{7}$$

the problem is posed as follows: it is required to find values of the constants C_0 and C_1 for which this approximate equality will be ensured. Suppose it is rigorously satisfied at a certain time t_* (we denote by α_* the values of the functions themselves at this point). From the condition that the two curves are tangent at $t = t_*$ it follows that the functions themselves and their first derivatives are equal

$$\left(\frac{\ln\dfrac{1}{1-\alpha_*}}{K}\right)^{1/n} = \frac{\ln\dfrac{1+C_0\alpha_*}{1-\alpha_*}}{C_1}, \tag{8}$$

$$K^{1/n} n \left(\ln\frac{1}{1-\alpha_*}\right)^{\frac{n-1}{n}} = \frac{C_1}{C_0+1}(1+C_0\alpha_*). \tag{9}$$

The simultaneous solution of (8) and (9) leads to a transcendental equation for C_0:

$$\frac{1+C_0\alpha_*}{1+C_0}\ln\frac{1+C_0\alpha_*}{1-\alpha_*} = n\ln\frac{1}{1-\alpha_*}, \tag{10}$$

which can be solved graphically or numerically for a fixed value of α_*.

In solving practical problems it is convenient to use the approximate analytic relations $C_0 = f_1(n)$ and $C_1 = f_2(K, n)$ to convert the constants of Eq. (1) into macrokinetic constants. This can be done most simply for $\alpha_* = 0.5$; then Eqs. (10) and (8) respectively take the form

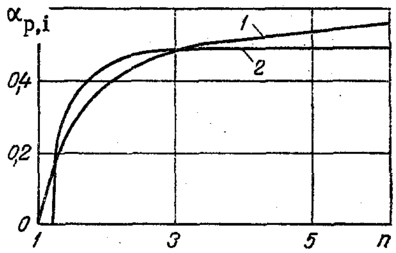

Fig. 3. Dependence of degree of crystallization $\alpha_{p.i.}$ on n at the point of inflection of the crystallization isotherm: 1) from Eq. (14); 2) from (15), using the analytic dependence of C_0 on n (12).

$$\ln(C_0+2)\frac{C_0+2}{C_0+1}=\ln 4^n,\quad C_1=\left(\frac{K}{\ln 2}\right)^{1/n}\ln(C_0+2). \tag{11}$$

The exact solution of system (11) is well approximated by the following analytic relations:

$$C_0=4^n-4, \tag{12}$$

$$C_1=\ln(4^n-2)\left(\frac{K}{\ln 2}\right)^{1/n}. \tag{13}$$

In order to represent possible divergences in this transformation, Fig. 2 shows curves plotted from Eq. (1) using $K_1 = 0.1$ min^{-2}, $n_1 = 2$, $K_2 = 0.1$ min^{-3}, $n_2 = 3$, $K_3 = 0.1$ min^{-4}, $n_3 = 4$, and curves calculated with the macrokinetic equations (6) with the constants C_0 and C_1 which appear in it determined with formulas (12) and (13), using the values given above for the constants in Eq. (1). In this special case, which is quite typical of many polymeric materials, Eq. (6) is valid (cf. Fig. 2) for all three curves with deviations from the curve plotted from Eq. (1) which are up to 1% in the range $0.2 \leqslant \alpha \leqslant 1.0$, and up to 80% in the range $0 < \alpha < 0.2$.

It is important also to compare the points of inflection on the theoretical crystallization isotherms obtained by using Eqs. (1) and (6), since the raw experimental data, as a rule, are the time dependences of the heat flux q(t), and consequently the position of such a characteristic of the process as the maximum rate of crystallization is quite well defined, of course within the limits of experimental error. From the condition $d^2\alpha/dt^2 = 0$ for Eq. (1) it is easy to obtain the following relations for $\alpha_{p.i}$ at the point of inflection of the crystallization isotherm:

$$\alpha^{*}_{p.i}=1-\exp\left(-\frac{n-1}{n}\right). \tag{14}$$

For Eq. (6) the formula which has the same meaning is

$$\alpha^{**}_{p.i}=0{,}5\left(1-\frac{1}{C_0}\right), \tag{15}$$

i.e. the position of the point of inflection predicted by the macrokinetic equation and by the Avrami–Kolmogorov equation is determined by the value of a single constant (C_0 or n). We now substitute the approximate value of C_0 from Eq. (12) into (15), and plot in Fig. 3 $\alpha^{*}_{p.i.}$ and $\alpha^{**}_{p.i.}$ against n calculated with Eqs. (14) and (15) respectively. Then for each of the values n = 2, 3, and 4 which we used in the mathematical model experiment, we determine from Fig. 3 the corresponding points $\alpha^{p.i.}_{14}$ and $\alpha^{p.i.}_{15}$, where the subscripts indicate the equation from which $\alpha_{p.i.}$ was calculated.

Using Fig. 2, and knowing $\alpha^{p.i.}_{14}$ and $\alpha^{p.i.}_{15}$, for each pair of curves, we find the time $t_{p.i.}$ corresponding to the position of the maximum on the thermokinetic curve (points on the figure). The divergence of the values of $t^{p.i.}_{14}$ and $p^{p.i.}_{15}$ for all three curves does not exceed 2%, which is no more than the experimental error.

In the present article we knowingly did not cite or discuss specific experimental data, first of all because there are extensive data in the literature which are described at least as well by Eq. (3) as by Eq. (1), and secondly because some examples of this kind are contained in our earlier papers [1, 2].

Thus, the analysis performed showed that a macrokinetic type equation describing the kinetics of a phase transition as an autocatalytic process is in as good agreement with experiment over the whole range of the degrees of transformations up to very high values as the widely known Avrami–Kolmogorov equation, and in the region of limiting degrees of transformation (as $\alpha \to 0$ and $\alpha \to 1$) is clearly better than the latter. An equation of the autocatalytic type is very much more convenient to use in solving nonisothermal problems.

NOTATION

α, degree of completion of heat release; t, time; K and n, Avrami constants; η, degree of crystallinity; α_e, equilibrium degree of crystallinity; A_1 and A_2, constants in macrokinetic equation; $\alpha_{p.i.}$, degree of completion of heat release at point of inflection of crystallization isotherm.

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HEATING OF A DOUBLE STEPPED PLATE BY A MOVING SOURCE

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Generalized functions and Fourier–Laplace integral transformation are used to derive the nonstationary temperature distribution and forces in a two-stepped plate heated by a moving source.

Consider an infinite thermally insulated plate heated by a moving line source of output q (Fig. 1). The thickness of the plate $2\delta(x)$ is represented by means of an unsymmetrical unit function in the form

$$\delta(x) = \delta_1 + (\delta_2 - \delta_1) S_+(x), \tag{1}$$

where

$$S_+(\zeta) = \begin{cases} 1, & \zeta > 0, \\ 0, & \zeta \leqslant 0. \end{cases}$$

We substitute (1) into the heat-conduction equation for a plate of variable thickness [1]

$$\Delta T + \frac{1}{\delta(x)} \frac{d\delta(x)}{dx} \frac{\partial T}{\partial x} = \frac{\dot{T}}{a} - Q\delta_+(x)\,\delta(y - V\tau)$$

and use the identity [2] $S_+(x)\delta_+(x) = \delta_+(x)$ to get

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