DEGREE OF CRYSTALLINE STRUCTURE OF POLYMER OBTAINED FROM MELT AT VARIOUS COOLING RATES

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An analytical dependence of the final degree of crystalline structure on the rate of temperature variation is obtained for polymer material. It is shown that the formula obtained ensures satisfactory agreement with experiment in a broad range of cooling rates.

In the real technological production of components from polymers which are crystallized from a melt, the crystallization always occurs in nonisothermal conditions, as a result of heat transfer with the surrounding medium and the low thermal conductivity in the bulk of the material. At the same time, it is well known that the structure of polymer (and other) materials and hence a whole set of their physical and mechanical properties depend on the cooling rate. In addition, even the degree of crystalline structure of the finished component depends on the cooling rate.

In nonisothermal polymer crystallization, specific kinetic phenomena arise as a result of the very nonlinear temperature dependence of the crystallization rate, on the one hand, and the relation between the heat loss to the surrounding medium and the heat input due to the existence of an internal heat source (the heat of crystallization), on the other.

The aim of the present work is to establish the relation between the cooling rate of the polymer material obtained from the melt and the final degree of crystal structure attained at the temperature at which crystallization no longer occurs. In fact, the temperature dependence of the crystallization rate takes the form in Fig. 1a. It is evident that \( \dot{\alpha} = 0 \) when \( T < T_C \) and the final degree of crystal structure \( \alpha_\infty \) attained at \( T < T_C \) depends on the rate of crossing the region from \( T_m \) to \( T_C \). In addition, it must be taken into account that, at any temperature in the range from \( T_m \) to \( T_C \), the equilibrium degree of crystal structure \( \alpha_e \) depends on the temperature, as shown schematically in Fig. 1b, but \( \alpha_e < 1 \) always.

A kinetic equation of the following form is used for quantitative description of crystallization

$$\frac{d\alpha}{dt} = K(T) \mu[\alpha, \alpha_e(T)].$$

(1)

For the sake of simplicity and clarity of the results obtained, polymer crystallization is considered in conditions of linear variation of the ambient temperature over time. Polymer crystallization in the interval $T_m - T_c$ is described using Eq. (1) in the form [1-3]

$$\frac{d\alpha}{dt} = k_0 \exp \left[ - \frac{U}{T - T_c} - \frac{\psi}{T_m - T} \right] (\alpha_e - \alpha)(1 + c_0\alpha).$$

(2)

The temperature dependence of the equilibrium degree of crystal structure is taken in the form [4]

$$\alpha_e(T) = a \left[ 1 - b \sqrt{\frac{T}{T_m - T}} \right],$$

(3)

which approximates the known experimental data sufficiently well. The kinetic constants used below for specific calculations characterize the crystallization of polycaproamide (PA-6) samples. The values of these constants are obtained by solving the inverse problem of nonisothermal kinetics [4] on the basis of extrapolation of the experimental data of [5] over the whole temperature range from $T_m$ to $T_c$: $a = 0.69$; $b = 0.11$; $k = 3.32 \text{ sec}^{-1}$; $U = 213.2 \text{ K}$; $\psi = 210.4 \text{ K}$; $c_0 = 42$; $T_c = 317 \text{ K}$; $T_m = 501 \text{ K}$.

To estimate the final degree of crystalline structure with linear temperature variation $T = T_m - vt$, the time derivative in Eq. (2) is replaced by the temperature derivative $d\alpha/dT = -v\alpha dt$, and integration over the whole temperature interval from $T_m$ to $T_c$ gives

$$\int_0^{\infty} \frac{d\alpha}{(\alpha_e - \alpha)(1 + c_0\alpha)} = \frac{\tau_c}{T_m} k_0 \exp \left[ - \frac{U}{T - T_c} - \frac{\psi}{T_m - T} \right] dT.$$

(4)

The analytical expression for the final degree of crystalline structure takes account of the following assumptions.

First, the chosen form of $k(T)$ permits sufficiently correct approximation by Taylor series expansion of the exponent. Retaining three terms of the expansion, the result obtained is

$$K(\Theta) = k_0 \exp \left[ - (\beta_1 + \beta_2) \Theta^2 \right],$$

(5)