Colloid Polym Sci 274:209–217 (1996)
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ORIGINAL CONTRIBUTION

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Crystallization of polymers in variable external conditions.

1. General equations

Received: 7 February 1995
Accepted: 11 September 1995

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Abstract A new model of crystallization kinetics in variable external conditions has been developed. The model concerns situations when temperature, pressure, stress, change in time. Compared to earlier models, the present treatment includes transient and athermal effects, proportional to the rate of change of the external conditions. The model can be used for simulation of crystallization in industrial processes (injection molding, fiber spinning, film blowing). The present paper offers general theoretical fundamentals of the model. Applications concerning more specific cases will be published separately.

Key words Crystallization – nucleation – growth – non-isothermal crystallization – thermal nucleation – athermal nucleation – transient effects – relaxation times

Introduction

Traditional studies of crystallization kinetics are limited to idealized conditions in which all parameters of state (temperature, pressure, etc.) are constants. In real situations, however, the conditions change in time, which makes crystallization rate dependent not only on the instantaneous conditions, but also on the rate of change.

The early models of crystallization in variable conditions concerned only variation of temperature, and that in the limit of slow cooling. The main object of this study is development of a tractable model of crystallization in variable external conditions, which could be used as an input to numerical simulation of polymer processing.

The generalization will concern two aspects. First, variable conditions other than temperature will be introduced. Second, athermal and transient effects will be considered. This paper contains general equations of the model, specification of necessary material functions, and general outline of experimental procedures leading to determination of non-isothermal crystallization characteristics. Detailed solutions concerning crystallization in variable temperature and/or stress conditions will be discussed in separate papers.

Variable crystallization conditions. Generalized non-isothermal processes

To describe crystallization conditions, we will consider a vector, Ψ, with components corresponding to individual parameters of state, such as temperature, T, pressure, p, intensity of an electric or magnetic field, $\mathscr{E}$, etc.

$$\Psi(t) = \{T(t), p(t), \mathscr{E}(t), \dots\} \ . \tag{1}$$

Instead of speaking, separately, about processes *non-isothermal* ($\partial T/\partial t \neq 0$), *non-isobaric* ($\partial p/\partial t \neq 0$), etc., we will use the term *non-isothermal* in a general sense, covering variation of any external conditions. A process will be defined as *non-isothermal* whenever the vector of conditions Ψ (any one of its components) change in time. A process will be considered *non-isothermal* also, when temperature is a constant, but some other parameter of state (e.g. pressure, or electric field) changes in time. This, generalized concept of non-isothermal processes, and the related generalized nucleation rates has been discussed earlier [1, 2].

Time variation of a physical characteristic, $\mathscr{X}$, controlled by time-dependent vector of external conditions $\Psi(t)$ with components Ψ_i, can be expressed through the rates of change, $\dot{\Psi}, \ddot{\Psi}, \ldots$

$$d\mathscr{X}[\Psi(t)]/dt = \dot{\Psi}\cdot(\partial\mathscr{X}/\partial\Psi) \equiv \sum_i (d\Psi_i/dt)(\partial\mathscr{X}/\partial\Psi_i) \quad (2a)$$

$$\begin{aligned} d^2\mathscr{X}[\Psi(t)]/dt^2 &= \ddot{\Psi}\cdot(\partial\mathscr{X}/\partial\Psi) + (\dot{\Psi}\otimes\dot{\Psi}):(\partial^2\mathscr{X}/\partial\Psi\,\partial\Psi) \\ &\equiv \sum_i (d^2\Psi_i/dt^2)(\partial\mathscr{X}/\partial\Psi_i) \\ &\quad + \sum_{i,j}\sum (d\Psi_i/dt)(d\Psi_j/dt)(\partial^2\mathscr{X}/\partial\Psi_i\,\partial\Psi_j) \end{aligned} \quad (2b)$$

$\dot{\Psi}, \ddot{\Psi}, \partial\mathscr{X}/\partial\Psi, \partial^2\mathscr{X}/\partial\Psi\,\partial\Psi$, are vectors or tensors in the space of external conditions, Ψ. $(\cdot)$ denotes scalar, and $(\otimes)$ dyadic product of two vectors, $(:)$ contraction of a pair of tensors over two indices, etc. For example, the rate of change of a steady-state nucleation rate, $\dot{N}_{st}$, which follows in time variation of temperature, pressure, and other conditions, can be written as

$$d\dot{N}_{st}[T(t), p(t), \ldots]/dt = (dT/dt)(\partial\dot{N}_{st}/\partial T) + (dp/dt)(\partial\dot{N}_{st}/\partial p) + \cdots \quad (3)$$

Crystallization at time t in the point r of the sample is controlled by *instantaneous, local conditions*, $\Psi(t, r)$. In the case of a *uniform field* of conditions ($\nabla\Psi = 0$), variation of Ψ experienced by a small part of the crystallizing material reduces to the *partial time derivative*

$$\nabla\Psi = 0; \qquad \dot{\Psi} = \partial\Psi/\partial t\,. \quad (4a)$$

When the distribution of temperature, stress, etc., in the sample is *non-uniform*, the effective rate of change is caused by local changes of Ψ, and by the motion of a material particle across the field of conditions, $\Psi(t, r)$. In non-uniform conditions, *material derivative* should be taken as the effective rate of change

$$\nabla\Psi \neq 0; \qquad \dot{\Psi} = \partial\Psi/\partial t + V\cdot\nabla\Psi\,, \quad (4b)$$

where $V(t, r)$ is local velocity of the material particle.

The fields of temperature, stress, and other variables are determined by dynamic equations describing the process. Time, and position-dependent crystallization rates, $\mathscr{K}[\Psi(t, r)]$ contribute additional dynamic equations which should be solved together with equations of continuity, momentum and energy.

The Kolmogoroff-Avrami equation of transformation

According to the model developed independently by Kolmogoroff [3], Avrami [4], Johnson and Mehl [5], and Evans [6], the relative degree of transformation (crystallinity), x, at a given time, t, reads

$$x(t) = 1 - \exp[-E(t)]\,; \quad (5)$$

$E(t)$ denotes volume fraction of "phantom crystals" grown up to time t

$$E(t) = N_0 v(0, t) + \int_0^t \dot{N}(s) v(s, t)\, ds\,, \quad (6)$$

N_0 is a number of predetermined crystal nuclei present at the start of the process ($t = 0$), $\dot{N}$ – nucleation rate, and $v(s, t)$ – volume of a phantom crystal, nucleated at the instant s and grown up to the instant t.

When the growth is isotropic and proceeds independently in n dimensions, v can be expressed by linear growth rate, $\dot{R}$

$$\begin{aligned} E(t) &= C_n N_0 \left[\int_0^t \dot{R}(z)\, dz\right]^n \\ &\quad + (C_n/(n+1)) \int_0^t \dot{N}(s) \left[\int_s^t \dot{R}(z)\, dz\right]^n ds\,, \end{aligned} \quad (7)$$

where C_n denotes shape factor.

In a general case, nucleation and growth rates are functions of time, and can possibly be affected by transient effects and the history of external conditions, $\Psi(t)$

$$\begin{aligned} \dot{N}(t) &= \dot{N}[t, \Psi(t)] \\ \dot{R}(t) &= \dot{R}[t, \Psi(t)] \\ E(t) &= E[t, \Psi(t)]\,. \end{aligned} \quad (8)$$

In isothermal conditions ($\Psi = \text{const}$), the kinetic characteristics can still be functions of time, and (constant) external conditions appear as parameters

$$\begin{aligned} \dot{N}(t) &= \dot{N}[t; \Psi] \\ \dot{R}(t) &= \dot{R}[t; \Psi] \end{aligned} \quad (8a)$$

and become constants only when, in addition to isothermal conditions, steady state is implied

$$\begin{aligned} \dot{N}(t) &= \text{const.} \\ R(t) &= \text{const.} \end{aligned} \quad (8b)$$

In such conditions Eq. (7) reduces to

$$E_{st}(t) = C_n \dot{R}^n t^n [N_0 + \dot{N}t/(n+1)]\,. \quad (9)$$

Equations (6), (7), and (9) combine two mechanisms of crystallization: growth of a constant number of predetermined nuclei, and sporadic formation of new nuclei followed by growth. The most popular form of steady-state, isothermal transformation equation (often called *Avrami equation*) is written for an isolated mechanism with a single, integer value of the exponent m

$$E_{\mathrm{st}}(t) = K_{\mathrm{m}} t^{\mathrm{m}} = \begin{cases} C_{\mathrm{n}} N_0 \dot{R}^{\mathrm{n}} t^{\mathrm{n}} & \text{for predetermined nucleation} \\ C_{\mathrm{n}} \dot{N} \dot{R}^{\mathrm{n}} t^{\mathrm{n}+1}/(n+1) & \text{for sporadic nucleation}\,. \end{cases} \tag{10}$$

In principle, non-isothermal crystallization processes can be described by Eqs. (6) or (7), provided that nucleation and growth rates are known functions of time. There remains an uncertainty about the exponent m, which in the original model is an integer constant, while it is commonly found to vary with temperature, stress, and other conditions. The present author discussed transformation equations with time-dependent exponents m, taken as step functions of the external conditions [7]; the variation of m with time is reasonable, but practical application of the results does not seem possible.

The main problem with using Eqs. (6) and (7) in real conditions concerns time-dependent nucleation and growth rates, and the dimensionality exponent, n. Experimental measurements usually yield isothermal crystallization rates and crystallization half-periods in a narrow range of external conditions, without detailed information about $\dot{N}(t)$, or $\dot{R}(t)$, taken separately. Isothermal measurements do not include any information about the effect of cooling rate or other time-dependent conditions.

Nevertheless, general scheme of the Kolmogoroff–Avrami model seems to provide a plausible basis for crystallization processes in variable conditions, and will be used, with small modification, in the development of our model.

Physical basis for nucleation and growth rates

The Kolmogoroff–Avrami equation provides a geometrical model of the development of the new phase. Physical basis for the material characteristics in Eqs. (7)–(10) is provided by nucleation theory, originally introduced by Volmer [8], Frenkel [9], Turnbull and Fisher [10]. Nucleation theory describes development of cluster size distribution density, $\varrho(g,t)$ determined by the Fokker–Planck equation derived from the kinetics of molecular aggregation

$$\frac{\partial \varrho}{\partial t} - \frac{\partial}{\partial g}\left[\mathscr{D}_{\mathrm{gr}}\left(\frac{\partial \varrho}{\partial g} + \frac{\varrho}{kT}\frac{\partial \Delta\tilde{F}}{\partial g}\right)\right] = 0\,. \tag{11}$$

Free energy, $\Delta\tilde{F}$, providing thermodynamic driving force for aggregation, and the growth–diffusion coefficient, $\mathscr{D}_{\mathrm{gr}}$, depend on external conditions, and in non-isothermal conditions become functions of time

$$\Delta\tilde{F}(\Psi) \to \Delta\tilde{F}[\Psi(t)]$$

$$\mathscr{D}_{\mathrm{gr}}(\Psi) \to \mathscr{D}_{\mathrm{gr}}[\Psi(t)]\,, \tag{12}$$

$\Delta\tilde{F}$ and $\mathscr{D}_{\mathrm{gr}}$ are controlled int. al., by heat of fusion, interface tension, molecular mobility, and other material properties.

Isolated values of physical characteristics appearing in $\Delta\tilde{F}$ and $\mathscr{D}_{\mathrm{gr}}$ have been measured for various polymers. The available information is restricted, however, to rather narrow range of external conditions, and scatters widely for each material. For example, melting temperatures reported for polypropylene range from 187 °C [11] to 208 °C [12]. Reported values of the heat of fusion, or interface tension, vary by 50% or more, and information about growth-diffusion rate is practically nonexistent. Many characteristics change with temperature, but quantitative information about their temperature relations is very scarce. Commonly assumed linear relation between free energy, $\Delta\tilde{F}$, and temperature is valid only for small undercoolings; wide range of temperatures involved in non-isothermal processes may require strongly non-linear relations. Rough estimates of the effect of molecular orientation and deformation suggest increase of nucleation rates by *many orders of magnitude* [13, 14], but experimental data are more than limited.

Equation (11) can be solved numerically for a variety of time-dependent conditions, to yield cluster density function, $\varrho(g,t)$, and the related kinetic characteristics appearing in the transformation equation. There are two difficulties, though. First, information about physical parameters of the nucleation theory is incomplete, inaccurate, and hard to obtain from direct measurements. Second, cluster density function, $\varrho(g,t)$, is not directly observable, and solutions of Eq. (11) cannot be verified experimentally. For these two reasons, formal solutions of the Fokker–Planck equation do not provide a good basis for a reliable non-isothermal kinetic model. We will use basic relations of the nucleation theory as hints for the construction of a simplified model, but quantitative evaluation will have to be based on direct experimental evidence.

Special features of non-isothermal crystallization

We will consider the non-linear measure of the degree of transformation (crystallinity) defined as

$$P(t) \equiv [-\ln(1-x)]^{1/m} = [E(t)]^{1/m} \in (0,\infty)\,, \tag{13}$$

where m is a constant. Time derivative of this function can be used as a measure of crystallization rate. dP/dt is inversely proportional to crystallization half-period, $t_{\frac{1}{2}}$, a characteristic which can be directly obtained from experiment

$$\mathscr{K} \equiv dP/dt = (\ln 2)^{1/m}(t_{\frac{1}{2}})^{-1} \,. \tag{14}$$

Equations (13)–(14) do not imply any specific combination of nucleation and growth, or constancy of external conditions. $\mathscr{K}$ depends on time as a result of transient effects, and time-dependent external conditions

$$\mathscr{K}(t) = \mathscr{K}[t, \Psi(t)] = \mathscr{K}[t, T(t), p(t), \ldots] \,. \tag{15}$$

In isothermal, steady-state, single-mechanism processes, $\mathscr{K}$ reduces to a constant, controlled by (constant) external conditions, Ψ

$$\mathscr{K}[t, \Psi(t)] \rightarrow \text{const.} = \mathscr{K}_{\text{st}}(\Psi) = \mathscr{K}_{\text{st}}(T, p, \ldots) \tag{16}$$

and the exponent m can be identified with the Avrami exponent in Eqs. (10).

In constant conditions ($\dot{\Psi} = 0$), crystallization is based solely on the growth of predetermined nuclei and/or *thermal nucleation* – a diffusional process leading to the formation of stable aggregates. In terms of one-dimensional nucleation theory and the generalized concept of a non-isothermal processes, the rate of thermal nucleation, $\dot{N}_{\text{th}}$, is equal to the flux of clusters in the space of cluster sizes, g (cf. Eq. (11) above)

$$\dot{N}_{\text{th}}[t, \Psi(t)] = -\mathscr{D}_{\text{gr}}[\partial\varrho/\partial g]_{g=g^*} \,, \tag{17}$$

$g^*(\Psi)$ denotes critical cluster size defining stable nuclei. It should be noted that thermal nucleation is present in constant, as well as in variable crystallization conditions.

In non-isothermal processes there appears an additional mechanism, absent in the conditions of constant temperature, or stress. *Athermal nucleation* consists in the "production" of stable nuclei by redefinition of the criterion of their stability. This concept has originally been introduced by Fisher, Hollomon and Turnbull [15], and later developed by the present author [2, 16]. The rate of athermal nucleation and the related contribution to crystallization rate, are proportional to the rate of change of the critical cluster size, g^*, which in turn, depends on the variation of external conditions

$$\begin{aligned}\dot{N}_{\text{ath}} &= -(dg^*/dt)\varrho(g^*) = -\dot{\Psi}\cdot(\partial g^*/\partial\Psi)\varrho[g^*(\Psi(t))] \\ &= -\left[\dot{T}\frac{\partial g^*}{\partial T} + \dot{p}\frac{\partial g^*}{\partial p} + \ldots\right]\varrho[g^*(\Psi(t))] \,.\end{aligned} \tag{18}$$

Consequently, in variable external conditions, nucleation and crystallization rates include two contributions, thermal and athermal.

In principle, athermal effects can appear in primary, as well as secondary nucleation (nucleation-controlled growth). From the nucleation theory result different values of the ratio $\dot{N}_{\text{ath}}/\dot{N}_{\text{th}}$ for primary (three-dimensional) and secondary (two-dimensional) nucleation. Writing

$$\dot{N}_{\text{ath}}/\dot{N}_{\text{th}} = \dot{\Psi}\cdot Z_3(\Psi) \tag{19a}$$

for primary, and

$$\dot{N}_{\text{ath}}/\dot{N}_{\text{th}} = \dot{\Psi}\cdot Z_2(\Psi) \tag{19b}$$

for secondary nucleation (nucleation-controlled growth), and realizing that the dimensionality of growth is n, we obtain athermal effect on the crystallization rate in the form

$$\mathscr{K}(t) = \mathscr{K}_{\text{th}}[(1 + \dot{\Psi}\cdot Z_3)(1 + \dot{\Psi}\cdot Z_2)^{n}]^{1/(n+1)} \tag{20}$$

It is evident that athermal contributions are proportional to the rate of change, and disappear when $\dot{\Psi} = 0$.

Early models of non-isothermal crystallization kinetics

The first, *quasi-static* model of non-isothermal crystallization was proposed by the present author [17]. In the original treatment, the only component of the vector Ψ was temperature, and m was assumed 1. Using the present, generalized approach, quasi-static model can be defined as one in which all parameters of state (temperature, pressure, stress, etc.) have been let to change in time, making steady-state crystallization rate $\mathscr{K}_{\text{st}}$ to follow variable external conditions

$$\mathscr{K}[t, \Psi(t)] \rightarrow \mathscr{K}_{\text{st}}[\Psi(t)] = \mathscr{K}_{\text{st}}[T(t), p(t), \ldots] \,. \tag{21}$$

Neglection of the transient effects implies that steady nucleation and growth rates are approached in a very short time. Integration of $\mathscr{K}_{\text{st}}$ over the history of external conditions, $\Psi(t)$, yields progress of transformation (crystallinity) in the form

$$P(t) = \int_0^t \mathscr{K}_{\text{st}}[\Psi(t')]\,dt' \,. \tag{22}$$

Another, *isokinetic model* was proposed by Nakamura, Watanabe, Katayama, and Amano [18, 19]. The model was based on the assumption of proportionality between the time-dependent rates of nucleation and growth

$$\dot{R}(t)/\dot{N}(t) = \text{const.} \tag{23}$$

It can be shown that the above assumption substituted into Eq. (7) yields

$$E(t) = C_1[\Phi(t)]^{n} + C_2[\Phi(t)]^{n+1} \,, \tag{24}$$

where $\Phi(t)$ is the integral

$$\Phi(t) = \int_0^t \dot{R}(t')\,dt' .$$

Proportionality between nucleation and growth rates does not follow from the theory, and provides a model assumption. The isokinetic assumption seems to imply steady-state, condition-dependent characteristics

$$\dot{R}(t) = \dot{R}_{st}[\Psi(t)]$$
$$\dot{N}(t) = \dot{N}_{st}[\Psi(t)] . \tag{25}$$

The assumption (23) substituted into Eq. (7) and reduced to a single nucleation mechanism, brings us back to the quasi-static model

$$E(t) = \mathrm{const.}\,[\Phi(t)]^{m} \Leftrightarrow P(t) = \int_0^t \mathscr{K}_{st}[\Psi(t')]\,dt' . \tag{26}$$

Wasiak [20] reviewed other models of non-isothermal crystallization. The early papers by Ozawa [21] and Borokhovskii [22] are based on the Kolmogoroff–Avrami treatment and employ the isokinetic and quasi-static assumptions. Somewhat different models, proposed by Sabsai [23] and Lee [24] cannot be reduced to the Avrami scheme. All the above models assume constant dimensionality of growth (if any), and neglect transient and athermal effects. Their attractiveness consists in that all necessary information is based on simple isothermal experiments, and is easily accessible. On the other hand, all the discussed models neglect transient and athermal effects inherent to non-isothermal conditions. The rate of change (e.g., cooling rate, $\dot{T}$) appears in the model only as a way of conversion of time, and does not affect crystallization rate.

In spite of drastic simplifications, the quasi-static and isokinetic model appeared to be quite successful in semi-quantitative analysis of slow non-isothermal processes [14, 17–19, 25].

The present author made two attempts to expand the quasi-static model onto higher cooling rates, but no satisfactory results have been obtained. The *proportional expansion* [7] suggested averaging of non-isokinetic nucleation and growth rates and admitted different growth rates in different crystallographic directions. The obtained series involved hard to find material functions. Generalization of the Avrami model introduced variable nucleation and growth mechanisms [7], but the functions $m(t)$ could hardly be predicted or measured.

In this study we propose a new model, which takes into account *transient* and *athermal* effects, and therefore can be applied in a wide range of variable conditions. The shape of many relations will be inferred from the theory of nucleation; restricted set of material characteristics must be found from experiments.

Extended equation for crystallization rates in variable external conditions

The quasi-static model will be completed with athermal and transient effects.

i) Crystallization rate, in isothermal conditions controlled solely by thermal nucleation, will be modified to account for athermal effects. Total crystallization rate will be approximated by

$$\mathscr{K}(t) = \mathscr{K}_{th} + \mathscr{K}_{ath} = \mathscr{K}_{th}[1 + \dot{\Psi}\cdot Z(t, \Psi(t))]^{\mu} . \tag{27}$$

The average vector Z, describes athermal effects resulting from nucleation and growth. Z_3 and Z_2 are (different) athermal functions for primary (three-dimensional) and secondary (two-dimensional) nucleation (cf. Eqs. (17–20)). Z_3, Z_2 are related to gradients of critical cluster sizes, $\partial g_i^*/\partial\Psi$. For each nucleation mechanism

$$\begin{aligned} Z_i &= (\partial g_i^*/\partial\Psi)\varrho[g_i^*, t, (\Psi(t))]/\mathscr{D}_{gr}[\partial\varrho/\partial g]_{g=g_i^*} \\ &= \left\{\frac{\partial g_i^*}{\partial T}, \frac{\partial g_i^*}{\partial p}, \dots\right\}\varrho[g_i^*(\Psi)]/\mathscr{D}_{gr}[\partial\varrho/\partial g]_{g=g_i^*}; \\ &\quad i = 2, 3 . \end{aligned} \tag{28}$$

When athermal effects are present, both, in primary nucleation and nucleation-controlled growth, and (in the spirit of isokinetic approximation), athermal corrections are assumed equal to each other ($Z = Z_3 = Z_2$), $\mu = 1$, and Eq. (27) reduces to

$$\mathscr{K}(t) = \mathscr{K}_{th}[1 + \dot{\Psi}\cdot Z] . \tag{27a}$$

There is no experimental evidence of athermal effects in crystal growth. When athermal mechanism is included only in primary nucleation, and growth is controlled solely by the thermal mechanism, $Z_2 = 0$, $Z = Z_3$, $\mu = (n+1)^{-1}$, and

$$\begin{aligned} \mathscr{K}(t) &= \mathscr{K}_{th}[1 + \dot{\Psi}\cdot Z]^{1/(n+1)} \\ &= \mathscr{K}_{th}\left[1 + \frac{1}{n+1}\dot{\Psi}\cdot Z(t, \Psi(t)) \right. \\ &\quad \left. - \frac{n}{(n+1)^2}(\dot{\Psi}\cdot Z)^2 + \cdots\right] . \end{aligned} \tag{27b}$$

The growth diffusion coefficient, $\mathscr{D}_{gr}$, appearing in the nucleation theory is proportional to molecular mobility (or reciprocal relaxation time, τ)

$$\mathscr{D}_{gr}(g, \Psi) = D_0 f_i(g)/\tau(\Psi) . \tag{29}$$

Consequently, athermal effects scale as $(\tau\,\dot{\Psi})$

$$\dot{N}_{ath}/\dot{N}_{th} = \dot{\Psi}\cdot Z = (\tau\,\dot{\Psi})\cdot(\partial g_i^*/\partial\Psi)\,h_i(t, g_i^*, \Psi) \tag{30}$$

f_i, k_i ($i = 2, 3$) are functions, different for two-dimensional, and three-dimensional nucleation.

ii) Transient effects associated with thermal-nucleation-controlled crystallization will be assumed in the form

$$d\mathcal{K}_{\mathrm{th}}/dt = \frac{\mathcal{K}_{\mathrm{st}}(\Psi(t)) - \mathcal{K}_{\mathrm{th}}(t, \Psi(t))}{\tau(\Psi(t))} . \tag{31}$$

Equation (31) may be considered as a relaxational solution truncated to one relaxation time, τ. The asymptotic behaviour at very long times and/or infinitely short relaxation times yields

$$\tau \to 0 \quad \text{and/or} \quad t \to \infty ; \qquad \mathcal{K}_{\mathrm{th}}(t) \to \mathcal{K}_{\mathrm{st}}(\Psi(t)) . \tag{32}$$

Crystallization rate asymptotically approaches steady-state value, corresponding to instantaneous conditions, $\Psi(t)$.

It should be understood that Eq. (31) is a postulated model, rather than result of a strict derivation. Our Fokker–Planck equation (11) admits relaxational solution

$$\varrho(g,t) = \sum_{\mathrm{i}} \varrho_{\mathrm{i}}(g) \exp[-t/\tau_{\mathrm{i}}] \tag{33}$$

reducing to

$$\frac{\partial \varrho}{\partial t} \cong \frac{\varrho_{\mathrm{eq}} - \varrho}{\tau_1} \tag{33a}$$

only above the critical transition temperature (melting temperature, T_{m}). In the infinite time limit, cluster sizes approach a Boltzmann-type, equilibrium distribution $\varrho_{\mathrm{eq}}(g)$. No such solution exists below T_{m}, though. The most natural solution of Eq. (11) below T_{m} is inherently time-dependent, because an irreversible, one-directional phase transition process is described. Nevertheless, in the majority of theoretical treatments (apparently inspired by constant nucleation rates observed in isothermal conditions), *steady state cluster distribution*, $\varrho_{\mathrm{st}}(g)$, independent of time, but controlled by external conditions is assumed below T_{m}.

The postulated relaxational equation (Eq. 31) is supported, to some extent, by the (assumed) existence of steady-state solution at $t \to \infty$, and proportionality of $\partial \varrho/\partial t$ to the growth-diffusion coefficient (reciprocal relaxation time, τ) implied by Eq. (11).

Equation (31) applied to non-isothermal conditions, $\Psi = \Psi(t)$, and integrated with the initial condition

$$t = 0; \qquad \mathcal{K}_{\mathrm{th}} = \mathcal{K}_0 \tag{34}$$

yields thermal crystallization rate

$$\mathcal{K}_{\mathrm{th}}(t) = e^{-\xi} \left[\mathcal{K}_0 + \int_0^{\xi} e^{\xi'} \mathcal{K}_{\mathrm{st}}[\Psi(\xi')] \, d\xi' \right] , \tag{35}$$

where

$$\xi(t) = \int_0^t \frac{dt'}{\tau[\Psi(t')]} \tag{36}$$

is a new time variable.

The constant $\mathcal{K}_0$, in Eq. (34) depends, in a general case, on structure and composition of the crystallizing material, and initial conditions, $\Psi(t = 0)$. In industrial processes (injection molding, extrusion, fiber spinning and melt blowing), which provide the main field of applications of our model, we are dealing with crystallization which follows prolonged melting. Ordered structures contributing to "crystallization memory" [26, 27] have to be destroyed at the beginning of the process, to guarantee reproducible material properties. Therefore, the absence of predetermined nuclei resulting from unmelted ordered structures can be taken for granted. What is left, is heterogeneous nuclei (impurities, pigments, etc.) resistant to melting. Crystallization characteristics of pure materials, free from predetermined (mostly heterogeneous) nuclei, may be different from crystallization of polymers containing pigments and impurities.

The integral appearing in Eq. (35) can be expanded in series of derivatives

$$\begin{aligned} \mathcal{K}_{\mathrm{th}}(t) - Ce^{-\xi} &= e^{-\xi} \int e^{\xi'} \mathcal{K}_{\mathrm{st}}[\Psi(\xi')] \, d\xi' \\ &= \mathcal{K}_{\mathrm{st}}[\Psi(\xi)] - d\mathcal{K}_{\mathrm{st}}/d\xi + d^2\mathcal{K}_{\mathrm{st}}/d\xi^2 \\ &\quad - \cdots + (-1)^{\mathrm{n}} d^{\mathrm{n}} \mathcal{K}_{\mathrm{st}}/d\xi^{\mathrm{n}} , \end{aligned} \tag{37}$$

where

$$C = \mathcal{K}_0 - [\mathcal{K}_{\mathrm{st}} - d\mathcal{K}_{\mathrm{st}}/d\xi + d^2\mathcal{K}_{\mathrm{st}}/d\xi^2 - \cdots]_{t=0} . \tag{38}$$

Differentiation with respect to ξ takes into account variation in time, scaled with relaxation time. Using Eqs. (1) and (2), Eq. (37) can be rewritten in the form indicating rates of change of the external conditions

$$\begin{aligned} \mathcal{K}_{\mathrm{th}}(t) - Ce^{-\xi} &= \mathcal{K}_{\mathrm{st}}[\Psi(t)] - \tau \dot{\Psi} \cdot (\partial \mathcal{K}_{\mathrm{st}}/\partial \Psi) \\ &\quad + \tau^2 (\dot{\Psi} \otimes \dot{\Psi}) : \left[\left(\frac{\partial \ln \tau}{\partial \Psi} \otimes \frac{\partial \mathcal{K}_{\mathrm{st}}}{\partial \Psi} \right) \right. \\ &\quad \left. + \frac{\partial^2 \mathcal{K}_{\mathrm{st}}}{\partial \Psi \partial \Psi} \right] + \tau^2 \ddot{\Psi} \cdot (\partial \mathcal{K}_{\mathrm{st}}/\partial \Psi) \\ &\quad - \tau^3 (\dot{\Psi} \otimes \dot{\Psi} \otimes \dot{\Psi}) : [\ldots] + \cdots \end{aligned} \tag{39}$$

In the range of $\dot{\Psi}$ low, compared with relaxation frequency, $(1/\tau)$, higher terms in Eq. (39) can be neglected.

The first term in Eqs. (37) and (39) describes steady-state crystallization rate which follows variable external conditions. Taken alone, this term corresponds to the *quasi-static* approximation (Eq. (20)).

Basic equation for the present model is provided by Eq. (35) corrected for athermal effects

$$\begin{aligned}\mathscr{K}(t) &= \mathscr{K}_{\mathrm{th}}[1 + \dot{\Psi}\cdot Z]^{\mu} \\ &= [1 + \dot{\Psi}\cdot Z]^{\mu}\left[\mathscr{K}_0 e^{-\xi} + e^{-\xi}\int_0^{\xi} e^{\xi'}\mathscr{K}_{\mathrm{st}}[\Psi(\xi')]\,d\xi'\right].\end{aligned} \tag{40}$$

Alternatively, Eq. (40) can be expanded in series around the *quasi-static* approximation. Using athermal nucleation vector, Z, from Eq. (28), and thermal crystallization rate from Eq. (39), we obtain

$$\begin{aligned}&\mathscr{K}(t) - Ce^{-\xi}(1 + \dot{\Psi}\cdot Z)^{\mu} \\ &= \mathscr{K}_{\mathrm{st}}[\Psi(t)]\left\{1 + \dot{\Psi}\cdot\left(\mu Z - \tau\frac{\partial\ln\mathscr{K}_{\mathrm{st}}}{\partial\Psi}\right)\right. \\ &\quad + (\dot{\Psi}\otimes\dot{\Psi}):\left[\frac{\mu(\mu-1)}{2}Z\otimes Z\right. \\ &\quad \left. + \tau^2\left(\frac{\partial\ln\tau}{\partial\Psi}\otimes\frac{\partial\ln\mathscr{K}_{\mathrm{st}}}{\partial\Psi}\right) + \tau^2\frac{1}{\mathscr{K}_{\mathrm{st}}}\frac{\partial^2\mathscr{K}_{\mathrm{st}}}{\partial\Psi\,\partial\Psi}\right] \\ &\quad \left. + \tau^2\ddot{\Psi}\cdot\left(\frac{\partial\ln\mathscr{K}_{\mathrm{st}}}{\partial\Psi}\right) + \tau^3(\Psi\otimes\Psi\otimes\Psi):[\ldots] + \cdots\right\}.\end{aligned} \tag{41}$$

Expansion over the rates of change may appear useful in the description of slow processes, and in the determination of athermal crystallization characteristics.

Material functions and their evaluation

Evaluation of the developed non-isothermal model requires knowledge of the following characteristics:

– steady-state crystallization rate, as a function of external conditions:

$$\mathscr{K}_{\mathrm{st}}(\Psi) = \mathscr{K}_{\mathrm{st}}(T, p, \ldots) \tag{42}$$

– relaxation time, as a function of external conditions

$$\tau(\Psi) = \tau(T, p, \ldots) \tag{43}$$

– athermal rate vector

$$Z(t, \Psi(t)) = Z(T, p, \ldots) \tag{44}$$

– history of the external conditions

$$\Psi(t, r) = \{T(t, r), p(t, r), \ldots\}\,. \tag{45}$$

Equations (42)–(44) describe *material functions*, Eq. (45) results from dynamics of the process, and will not be discussed here. The first material function, $\mathscr{K}_{\mathrm{st}}$, is a characteristic of steady-state, isothermal crystallization and can be determined in standard laboratory experiments. Relaxation time, τ, appears in isothermal, transient conditions, and the athermal characteristic, Z requires controlled non-isothermal experiments.

There are two possible sources of information about the material functions $\mathscr{K}_{\mathrm{st}}$, τ, and Z. One is provided by *physical theories* (nucleation theory, molecular dynamics, etc.), yielding an *a priori* information about crystallization rates, relaxation times and athermal effects. Whenever possible, we will use such an approach to analyze *shapes of relations* and their asymptotic behavior. Using physical theories, we still need reliable values of material characteristics. These must be found from appropriate experiments.

The other source is *empirical*. The relations between material characteristics and external conditions are approximated by empirical equations, and evaluated from direct experiments. Empirical relations have to be introduced, whenever reliable physical equations are not available.

Two special crystallization regimes can be used for experimental determination of the necessary materials characteristics. Dependently on the available experimental techniques, transformation rate, $\mathscr{K}$, and/or degree of transformation, P, can be used.

Isothermal crystallization

In strictly isothermal conditions

$\Psi(t) = \mathrm{const.}$
$\mathscr{K}_{\mathrm{st}} = \mathrm{const.}$
$\tau = \mathrm{const.}$

athermal effects disappear, and crystallization rate from Eq. (40) reduces to

$$\mathscr{K}(t;\Psi) = (\mathscr{K}_0 - \mathscr{K}_{\mathrm{st}})e^{-t/\tau} + \mathscr{K}_{\mathrm{st}}\,. \tag{46}$$

The non-linear degree of transformation

$$P(t;\Psi) = \mathscr{K}_{\mathrm{st}}(t - \tau) + \mathscr{K}_0\tau + (\mathscr{K}_{\mathrm{st}} - \mathscr{K}_0)\tau\, e^{-t/\tau}\,. \tag{47}$$

Steady state transformation (crystallization) rates may be obtained from the asymptotic behavior of Eq. (46) at $t \to \infty$

$$\mathscr{K}_{\mathrm{st}}(\Psi) = \lim_{t\to\infty}\mathscr{K}(t;\Psi) \tag{48}$$

and relaxation time, from the slope

$$[\tau(\Psi)]^{-1} = d\ln[\mathscr{K}_{\mathrm{st}}(\Psi) - \mathscr{K}(t;\Psi)]/dt\,. \tag{49}$$

Crystallization at constant rate of change

Determination of the athermal correction, Z, requires experiments performed at the controlled, constant rate of change

$\dot{\Psi} = \text{const.}$

$\ddot{\Psi} = \dddot{\Psi} = \cdots = 0.$

Using first terms of the expansion (41), we obtain the equation

$$\lim_{\dot{\Psi} \to 0} \frac{\partial \ln \mathscr{K}(t)}{\partial \dot{\Psi}} = \mu(Ce^{-\xi} + \mathscr{K}_{\mathrm{st}}[\Psi(t)])Z - \tau \frac{\partial \mathscr{K}_{\mathrm{st}}}{\partial \Psi}\,, \tag{50}$$

which can be used for determination of the athermal vector, Z. Detailed procedures for determination of Z in specific situations will be discussed in other papers.

Discussion

The difference between the present model and the original *quasi-static* approximation is threefold:

- variation of a single variable – temperature – is generalized onto many external conditions relevant for crystallization: temperature, pressure, external potential fields, etc. This generalization is specially important for processes in which polymers are subjected to mechanical and thermal stresses, resulting in molecular orientation and deformation.
- instead of *steady-state, isothermal* nucleation and growth characteristics used in the early models, we are considering *transient* effects related to the behavior in variable external conditions. The appropriate measure of such effects is *relaxation time*, τ, inversely proportional to the coefficient of growth diffusion, $\mathscr{D}_{\mathrm{gr}}$. In rate expansions, τ appears together with the rate of change, $\dot{\Psi}$.
- total nucleation (and crystallization) rates include, in addition to thermal nucleation considered in the earlier models, also *athermal nucleation*, directly proportional to the rate of change, $\dot{\Psi}$.

We will discuss asymptotic behavior of *crystallization rate*, $\mathscr{K}$, and *crystallinity*, P, in the range of very small, and very large values of the parameter $(\tau|\dot{\Psi}|)$.

At $(\tau|\dot{\Psi}|) \to 0$, i.e., for nearly constant conditions and/or infinitely short relaxation times, Eq. (41) reduces to the quasi-static model. Transient and athermal effects disappear, and crystallization rate assumes the steady-state value, $\mathscr{K}_{\mathrm{st}}$, corresponding to instantaneous conditions

$$(\tau|\dot{\Psi}|) \to 0; \qquad \mathscr{K}(t) = \mathscr{K}_{\mathrm{st}}(\Psi(t)) \propto 1/\tau\,. \tag{51}$$

Since crystallization rate is inversely proportional to relaxation time, (cf. Eqs. (17 and 29)), at $\tau \to 0$ crystallization rates become infinitely high. The crystallinity function P, assumes infinitely high values at either $\tau \to 0$, or $\dot{\Psi} \to 0$

$$(\tau|\dot{\Psi}|) \to 0; \qquad P(t) = \int \mathscr{K}_{\mathrm{st}}(\Psi(t))\,dt \propto 1/(\tau|\dot{\Psi}|) \to \infty \tag{52}$$

equivalent to complete transformation ($x \to 1$). $|\dot{\Psi}|$ appears in the integral (52) when integration over time is replaced by integration over external conditions. This is consistent with conclusions drawn from the original quasi-static and isokinetic models [17–19, 21–22] in which crystallinity function P was inversely proportional to the cooling rate, $\dot{T}$.

When the rate of change, and/or relaxation time, are infinitely large, nucleation (and crystallization) mechanism reduces to athermal

$$(\tau|\dot{\Psi}|) \to \infty; \qquad \mathscr{K}(t) \to \mathscr{K}_{\mathrm{ath}} = \mathscr{K}_{\mathrm{th}}(\dot{\Psi} \cdot Z)^{\mu}\,. \tag{53}$$

Thermal crystallization rate is proportional to $(1/\tau)$ and the athermal vector Z to τ (Eq. (17). Therefore, at $(\tau|\dot{\Psi}|) \to \infty$

$$\mathscr{K}(t) \propto (|\dot{\Psi}|)^{\mu} \cdot (\tau)^{\mu - 1}\,. \tag{54}$$

Assuming that athermal effects are present only in primary nucleation, and growth is solely controlled by thermal (diffusional) effects, i.e., putting

$$\mu = 1/(n+1) < 1\,, \tag{55}$$

we have

$$\mathscr{K}_{\mathrm{ath}}(\Psi, \dot{\Psi}) \propto \begin{cases} |\dot{\Psi}|^{1/(n+1)} \to \infty & \text{for finite } \tau \\ \tau^{-n/(n+1)} \to 0 & \text{for finite } |\dot{\Psi}|\,. \end{cases} \tag{56}$$

When τ, and growth rate are finite, crystallization rate slowly but infinitely increases with the rate of change, $\dot{\Psi}$. The infinite limit accounts for fast production of athermal nuclei (proportional to $\dot{\Psi}$), followed by finite rate of growth. When cooling rate is moderate, but relaxation time infinite (zero molecular mobility), crystallization rate reduces to zero because athermal nuclei fail to grow.

At $(\tau|\dot{\Psi}|) \to \infty$ the crystallinity function, P, reduces to zero

$$(\tau|\dot{\Psi}|) \to \infty : P \to \int \mathscr{K}_{\mathrm{ath}}(\Psi, \dot{\Psi})\,dt \propto (\tau|\dot{\Psi}|)^{-(m-1)/m} \to 0 \tag{57}$$

as a result of both, zero growth rate, and infinitely short time available for crystallization.

The model will be applied to crystallization processes with variable temperature, pressure, stress and other conditions. It should be made clear that the vector of external conditions $\Psi(t)$ is understood as *an effective, local value*, rather than *boundary value* applied to a large system. Crystallization rate equations discussed in this paper, $\mathscr{K}[t, \Psi(t), \dot{\Psi}(t)]$, play the role of *constitutive equations*

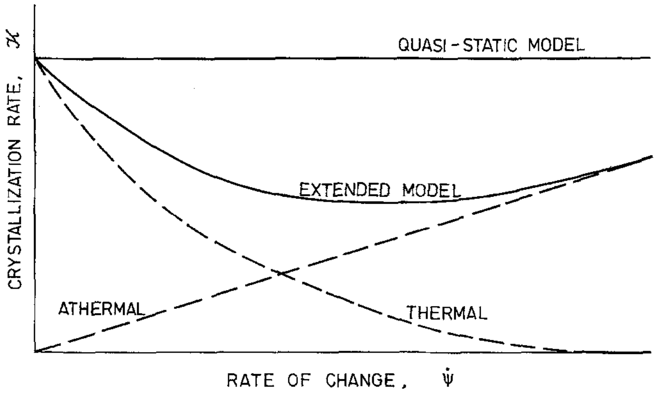

Fig. 1 Non-linear crystallization rate, $\mathscr{K}$, as a function of the rate of change, $|\dot{\Psi}|$ (schematic). Continuous lines – quasi-static and the extended models. Dotted lines – thermal and athermal components of the extended model. The rates are compared at the same conditions, Ψ

with effective conditions Ψ taken as local parameters. Non-uniform distribution of Ψ (e.g., temperature) in large systems, should be found from dynamic equations (e.g., heat transfer equation) and appropriate boundary conditions. Modeling of industrial processes, like injection molding or fiber spinning, is based on simultaneous dynamic equations, which determine, int. al. time evolution and spatial distribution of physical conditions, $\Psi(r, t)$. Development of crystallinity is one element of the dynamic model.

Figure 1 presents schematically behavior of crystallization rate, $\mathscr{K}$, in generalized non-isothermal conditions, as a function of the rate of change, $|\dot{\Psi}|$. Constant rate predicted in the old, quasi-static model is replaced by a complex relation resulting from decreasing transient thermal crystallization and increasing athermal contribution.

It is not possible to give a detailed recipe of application of the model in a general case. An outline of material functions required and their derivation from isothermal and non-isothermal experiments has been sketched in Eqs. (42–50). In the following papers we will discuss in detail application of the model to more specific (and simple) cases, for which there exists enough information about crystallization rates. The first such case, to be published soon, will be crystallization in which temperature is the only time-dependent variable.

Acknowledgment This work has been supported in part by Research Grant #PB 1291/S2/93/04 offered by the Committee of Scientific Research (Komitet Badań Naukowych).

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