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Wide angle X-ray scattering studies of transient effects in non-isothermal crystallization of *i*-polypropylene

Andrzej Wasiak*

Technical University of Bialystok, Wiejska 45A, 15-351 Bialystok, Poland

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Abstract

Crystallization behaviour of *i*-polypropylene in non-isothermal conditions was studied by means of WAXD using monochromatised X-ray synchrotron radiation. It is demonstrated that the crystallization rate during continuous cooling with a constant rate is not only a function of actual, momentary temperature, but also depends on the cooling rate. Near the melting temperature, the measured values of non-isothermal crystallization rate are close to those evaluated from isothermal crystallization, while at lower temperatures the difference between both quantities increases substantially. Interpretation of the results, based on Ziabicki's model of crystallization kinetics, offers a new approach leading to the estimation of relaxation time characterising the transient course of crystallization. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Non-isothermal crystallization; Synchrotron radiation; X-ray scattering

1. Introduction

Understanding of crystallization behaviour of polymers in variable external conditions appears more and more important from both fundamental as well as practical points of view. This concerns variations of temperature, pressure or stress that might occur during the phase transition. The present paper, following the preliminary reports [1–7], is focused on crystallization processes occurring in non-isothermal conditions, i.e. in the situation when the temperature of the material is forced to vary during the transition.

Studies on crystallization of polymers, carried out for many years, have been focused on isothermal conditions, normally achieved by melting of the polymer sample at a temperature well above the equilibrium melting point followed by rapid quenching to the crystallization temperature T_c. The kinetics of the transition have been usually described by means of the equation simplified from the more general theory proposed by Avrami [8–10]. Besides the isothermal studies, a number of authors [11–15] introduced several non-isothermal methods for studying the crystallization kinetics, cf. [16,17]. A review, made by the present author [16], has shown that these methods either employ a so-called 'isokinetic' approximation, or the assumption of a quasistatic course of the process; both cases leading to the conclusion that the isothermal and non-isothermal crystallization courses can be described by means of same characteristics. The same approach was also used in several papers published later [18–22]. The new model, introduced by Ziabicki [25,26], offers an extension of the classical theory introducing effects connected to the deviations from the isokinetic behaviour. The present paper is devoted to the experimental determination of some characteristics resulting from Ziabicki's model.

1.1. Models of crystallization kinetics

Classical approach to the description of crystallization kinetics was introduced by Ziabicki [11,15] and Nakamura et al. [13,14] relating the crystallization progress, $x(t)$, in non-isothermal conditions to the temperature dependence of the crystallization rate:

$$x(t) = 1 - \exp\left(-\left[\int_0^t K(T(s))\mathrm{d}s\right]^n\right) \tag{1}$$

where $K(T) = k(T)^{1/n}$, n is the Avrami exponent, s is the current time, and $k(T)$ is the isothermal rate constant.

It was experimentally demonstrated [3,7,23] that Eq. (1) cannot offer adequate description of the course of crystallization in the real, non-isothermal conditions, and as a

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* Address: Institute of Fundamental Technological Research, Polish Academy of Sciences, Swietokrzyska 21, 00-049 Warszawa, Poland. Tel.: +48-22-826-12-81; fax: +48-22-826-98-15.

E-mail address: awasiak@ippt.gov.pl (A. Wasiak).

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consequence, the use of more sophisticated, generalised model should be attempted.

The most pronounced factor that causes deviations from the isokinetic or quasi-static course of the process, is a memory exhibited by a polymer. It concerns a memory of the previous structure, or a memory of the history of external conditions experienced by the sample. Its existence leads to transient effects. The memory of spherulitic structure was known long ago and has been frequently discussed. Recently, memory effects were also discovered in the crystallization kinetics [24]. Rather long relaxation times with high activation energy were determined [24] as characteristics of the observed phenomenon.

A kinetic model of non-isothermal crystallization, taking into account the possible deviations from quasi-static or isokinetic courses of the process, has recently been offered by Ziabicki [25,26]. Besides the effects related to the relaxation time, deviations from the isokinetic behaviour are caused by athermal nucleation. The notion of athermal nucleation denotes the appearance of nuclei formed from unstable subcritical fluctuations as a result of a decrease of critical radius $r^*(T)$ with a decrease of temperature, rather than due to an increase of their size. In contrast, the thermal nucleation is achieved by the growth of aggregates to the size larger than some (constant) critical radius.

According to Ziabicki [25], the rate of athermal nucleation is a function of cooling rate. The theory of transient, non steady-state course of the process [25,26], characterised by some value of relaxation time, accompanied also by athermal nucleation, predicts crystallization rate being dependent not only on the actual values of the state parameters, but also on the rate of their change, e.g. dependent not only on temperature, but also on the cooling rate.

The model is represented by the equation in the form:

$$K(t) = [1 - \dot{T}B_{\mathrm{ath}}]^{1/n}\left[K_0 \mathrm{e}^{-\zeta} + \mathrm{e}^{-\zeta}\int_0^{\zeta} \mathrm{e}^{\zeta'} K_{\mathrm{st}}[T(\zeta')]\mathrm{d}\zeta'\right] \tag{2}$$

where $n = m + 1$ is the Avrami exponent and m is a geometric constant (representing the dimensionality of growth). The value 1 included in the Avrami exponent represents the sporadic nucleation considered in the theory. $\zeta(t) = \int_0^t \mathrm{d}t'/\tau[T(t')]$ is a new time variable, $K_{\mathrm{st}}(T)$ is the steady-state crystallization rate, $\tau(T)$ is the relaxation time, and $B_{\mathrm{ath}}(T)$ the athermal rate function.

A detailed discussion of the physical meaning of these parameters has been given by Ziabicki [25,26].

Eq. (2) can be written in the form [27]

$$K(t) = [1 - \dot{T}B_{\mathrm{ath}}]^{1/n}[K_{\mathrm{th}}] \tag{2a}$$

indicating the thermal K_{th} and athermal B_{ath} contributions to the crystallization rate.

Crystallization progress is expressed [25,26] by a new, non-linear measure

$$P \equiv [-\ln(1 - x)]^{1/n} = \frac{1}{\dot{T}}\int_{T_0}^{T} K(T')\mathrm{d}T' \tag{3}$$

Expansion of the thermal K_{th} and athermal B_{ath} functions into series and neglecting the terms higher than the first one, leads to the expression which for the case of constant cooling rate, $\dot{T}$, gives the function $P[T(t)]\dot{T}$ in a form:

$$P[T(t)]\dot{T} = -\int_{T(t)}^{T(0)} K_{\mathrm{st}}(T')\mathrm{d}T' - \dot{T}\int_{T(t)}^{T(0)} (A_1(T') + B_1(T'))K_{\mathrm{st}}(T')\mathrm{d}T' \tag{4}$$

where K is the total crystallization rate, K_{st} is the steady-state crystallization rate, $T(0)$ is the starting temperature, $T(t)$ is the upper crystallization temperature at time t, $A_1(T)$ is a function describing the transient effects with the relaxation time τ, and $B_1(T)$ is an athermal function. The temperature dependent coefficients $A_1(T)$ and $B_1(T)$ are given as [25–27]:

$$A_1 = -\tau(\partial \ln K_{\mathrm{st}}/\partial T) \tag{5}$$

$$B_1 = -\frac{B_{\mathrm{ath}}}{n} = \frac{-48(\pi/n)\sigma^3 T_{\mathrm{m}}^2}{kT\Delta T^3 \Delta h^2}\tau \tag{6}$$

where σ is the average interface tension of *i*-polypropylene crystal, $\Delta T = T_{\mathrm{m}} - T$ the undercooling, T_{m} the melting temperature, τ the effective relaxation time (the symbol τ^* is used in the original paper [25,26]), and Δh the heat of fusion.

Ziabicki's model [25–27] offers several possibilities of experimental determination of the kinetic characteristics. The crystallization rate as a function of temperature and cooling rate can be determined directly from the crystallization progress in the non-isothermal experiment:

$$K(T, \dot{T}) = -\frac{\mathrm{d}(-P\dot{T})}{\mathrm{d}T} \tag{7}$$

On the other hand, the asymptotic behaviour of the dependence $-\dot{T}P(t)$ vs. $-\dot{T}$ can be used to evaluate [26,27] several characteristics of the process, i.e.

$$\lim_{\dot{T}\to 0} (-\dot{T}P) = \int_{T(t)}^{T(0)} K_{\mathrm{st}}(T')\mathrm{d}T' \tag{8}$$

When Eq. (8) is applied to several temperatures $T(t)$, the temperature dependence of the steady-state crystallization rate can be determined as:

$$K_{\mathrm{st}}(T) = -\frac{\mathrm{d}}{\mathrm{d}T}\lim_{\dot{T}\to 0} (-\dot{T}\cdot P) \tag{9}$$

The initial slope of the same dependence $-\dot{T}P(t)$ vs. $-\dot{T}$,

$$\lim_{\dot{T}\to 0} \frac{\mathrm{d}(-\dot{T}P)}{\mathrm{d}(-\dot{T})} = \int_{T(t)}^{T(0)} K_{\mathrm{st}}(T')(A_1(T') + B_1(T'))\mathrm{d}T' \tag{10}$$

is related to the sum of relaxation and athermal effects, and consequently the sum of appropriate coefficients equals:

$$A_1(T) + B_1(T) = \frac{1}{K_{\mathrm{st}}(T)}\frac{\mathrm{d}}{\mathrm{d}T}\left[\lim_{\dot{T}\to 0}\frac{\mathrm{d}(-\dot{T}P)}{\mathrm{d}(-\dot{T})}\right] \tag{11}$$

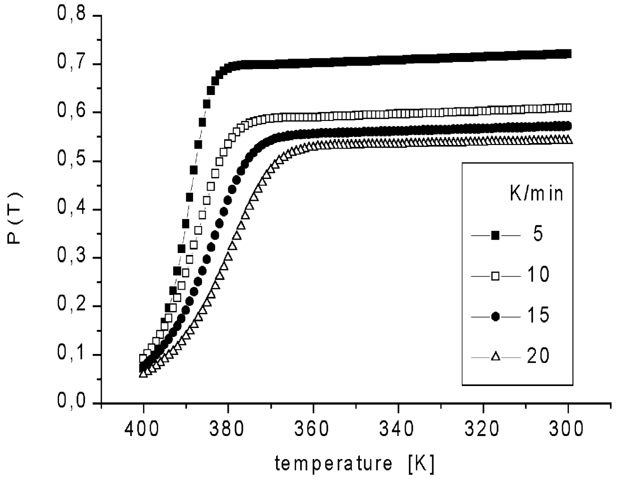

Fig. 1. Crystallization progress $P(T)$ for non-isothermal processes with different cooling rates expressed as a function of decreasing temperature.

2. Experimental

An isotactic polypropylene (*i*-PP) manufactured by Himont (Miland, Italy) with $M_w = 476 \times 10^3$ and $M_w/M_n = 6$ was used. It is the same sample as used by Alfonso and Ziabicki [24], and by Piccarolo [28]. The polymer sample was melted in the oven placed in the vacuum path of the instrument. Melting was followed by linear cooling with rates in the range of 5–20 K/min.

The studies on crystallization were carried out by means of time resolved wide angle X-ray diffraction using synchrotron radiation (DESY-HASYLAB, A2). The intensity of scattered radiation was recorded by means of a linear position sensitive detector. The range of scattering angles covering the Bragg spacings between 0.3 and 0.65 nm was divided onto 512 equidistant channels. The period of non-isothermal experiment was divided onto 128 frames (10 s each) separated by a time interval dependent upon the total time of cooling (dependent on the cooling rate).

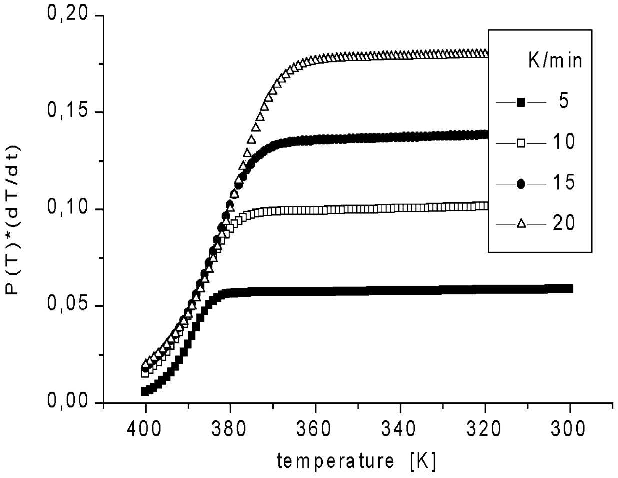

Fig. 2. The product $P[T(t)]\dot{T}$ as a function of decreasing temperature in non-isothermal crystallization processes with different cooling rates.

The integral intensities of the 130 and 040 reflections of the α form and 300 reflection of the β form (cf. [29]) were separated from the distribution of scattered radiation. Three characteristics were determined to represent the crystallization progress as a function of time:

$$C_\alpha = (I_{\alpha 130} + I_{\alpha 040})/I_a, \qquad C_\beta = I_{\beta 100}/I_a, \qquad \text{and} \qquad C_{TOT} = (I_{\alpha 130} + I_{\alpha 040} + I_{\beta 100})/I_a \tag{12}$$

where I_a is the integral intensity of the halo obtained from the molten sample. The characteristics mentioned above, calculated as functions of time, were applied for the further analysis of crystallization behaviour. The measured crystallinity as a function of time was further converted to the dependence on temperature, and fitted to the function:

$$\Phi(T) = \begin{cases} (A1 - A2)/\{1 + \exp((T - T0)/\Delta T)\} + A2 & \text{if} \quad T < T' \\ a + (T - T')\varphi & \text{if} \quad T > T' \end{cases} \tag{13}$$

where T' is an arbitrarily chosen transition temperature between the sigmoidal and linear increase of crystallinity, and all other parameters are the fit variables. An excellent accuracy of the fit was achieved for each cooling rate.

In order to convert crystallinity $x(T)$ to $P(T)$ according to Eq. (3), it is necessary to accept some value of the Avrami exponent n. (It seems to be a weak point of the theory so far developed.) Isothermal experiments, performed on the same instrument, gave for several temperatures the value of Avrami exponent close to $n = 2,6$. In order to be close to a physically meaningful value, in this paper calculations were performed with $n = 3$. It was, however, checked that the eventual acceptance of the experimentally measured isothermal value would cause only a small change of numerical results without affecting the shapes of relationships being derived.

3. Results

Development of crystallinity $P(T)$ of the α-form expressed as a function of temperature during cooling with various rates is presented in Fig. 1.

A rapid increase of crystallinity is observed in the initial period of time (high temperatures). At any temperature, the actual crystallinity depends on the cooling rate. The temperature range of crystallization is affected by the cooling rate. The higher the cooling rate the lower is the temperature at which the crystallization terminates. The final degree of crystallinity also decreases with an increase of cooling rate. Similar behaviour is also observed for the β crystal form. No transition between α and β forms was observed.

A plot showing changes of $P[T(t)]\dot{T}$ for the α-form with temperature during non-isothermal process is shown in Fig. 2. The individual curves of the plot correspond to different cooling rates. The product $P[T(t)]\dot{T}$ at a given

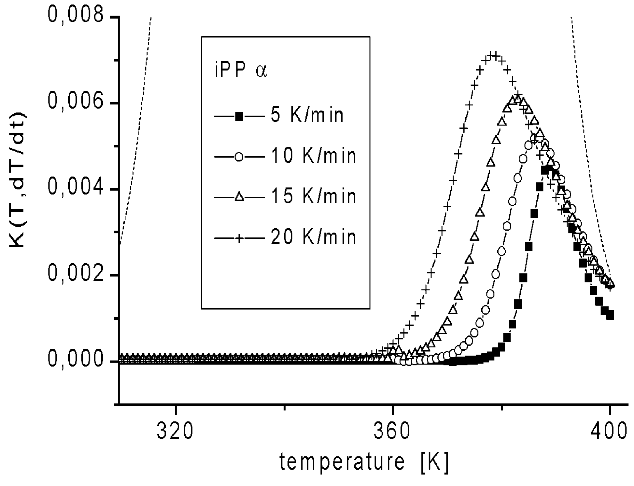

Fig. 3. Crystallization rate exhibited by *i*-polypropylene at several constant rate cooling processes, compared to the temperature dependence of isothermal crystallization rate.

temperature is also a function of the cooling rate. Application of Eq. (7) leads to the temperature dependence of the crystallization rate presented in Fig. 3. For each cooling rate a different course of crystallization rate K upon temperature is observed. Each curve shows a maximum at a certain temperature. The increase of cooling rate results in a shift of the maximum towards lower temperatures and in an increase of the value of crystallization rate at the maximum. Except for high temperatures, the non-isothermal crystallization rates are much lower than the isothermal ones, given by a dotted curve representing the data determined by means of Eq. (14) for *i*-polypropylene proposed by Hieber [17] in the form:

$$K_{\mathrm{iso}}(T) = \exp[-(B_1 + B_2 T + B_3 T^2)] \qquad (14)$$

with numerical constants [17] $B_1 = 12.28$, $B_2 = -0.3691/°\mathrm{C}$, and $B_3 = 0.002276/°\mathrm{C}^2$. The temperature scale was later converted to K. An agreement of the above data with some own isothermal data was also checked.

4. Discussion

Analysis of the X-ray diffraction data performed earlier [1–7] using Eqs. (9) and (11) as described by Ziabicki [26,27], have not given satisfactory determination neither of K_{st} and the coefficient $A_1 + B_1$ nor the relaxation time τ. The reason was connected to the uncertainty in the extrapolation of the experimental data to zero cooling rate.

The present analysis is based upon the assumption that the steady state crystallization rate is equal to that measured in isothermal conditions. This assumption, except the eventual numerical difference, is equivalent to the assumption that there exists some steady-state crystallization rate, constituting a limit to which the functions $K(T, \dot{T})$ converge at $\dot{T} \longrightarrow 0$. This function is only temperature dependent and is independent of the cooling rate. In order to perform analysis, an integral of the function $K_{\mathrm{iso}}(T)$ was calculated of the form given below:

$$C_{\mathrm{iso}}(T) = \int_{T_0}^{T} K_{\mathrm{iso}}(T')\mathrm{d}T' \qquad (15)$$

Replacing the first integral in Eq. (4) by $C_{\mathrm{iso}}(T)$, and after small rearrangements one obtains:

$$\frac{-P[T(t)]\dot{T} - C_{\mathrm{iso}}(T)}{\dot{T}} = \int_{T(t)}^{T(0)} (\tilde{A}_1(T') + \tilde{B}_1(T'))K_{st}(T')\mathrm{d}T' \qquad (16)$$

Further, by replacing K_{st} by K_{iso} in Eq. (16), the sum of hypothetical coefficients describing the athermal and transient effects is obtained:

$$\tilde{A}_1(T') + \tilde{B}_1(T') = \frac{1}{K_{\mathrm{iso}}(T')} \frac{\mathrm{d}}{\mathrm{d}T}\left[\frac{-P[T(t)]\dot{T} - C_{\mathrm{iso}}(T)}{\dot{T}}\right] \qquad (17)$$

The plot representing the left side of Eq. (16) obtained from the values $P(T)$ measured at different cooling rates is shown in Fig. 4. It shows the temperature dependence of the integral in Eq. (16), which depends not only on the temperature but also on the cooling rate. Values for different cooling rates are almost equal at high temperatures and substantially differ at lower temperatures. The higher the cooling rate the lower is the saturation value of $(-P(T)\mathrm{d}T/\mathrm{d}t - C_{\mathrm{iso}})$ divided by $\mathrm{d}T/\mathrm{d}t$.

Obviously, the region of high temperatures correspond to the beginning of crystallization, while at lower temperatures, where saturation is achieved, the more advanced stage of the transition occurs.

Fig. 5, in turn, shows hypothetical coefficients $\tilde{A}_1$ and $\tilde{B}_1$ obtained through application of Eq. (17). The sum of coefficients $\tilde{A}_1$ and $\tilde{B}_1$ depends on both the temperature and the

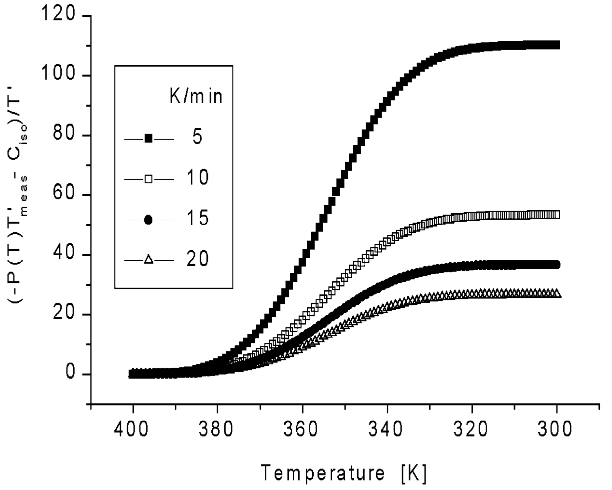

Fig. 4. Divided by dT/dt and expressed as a function of temperature, differences between values of the product $-P(T)\mathrm{d}T/\mathrm{d}t$, measured at various cooling rates, and values of $C_{\mathrm{iso}}(T)$.

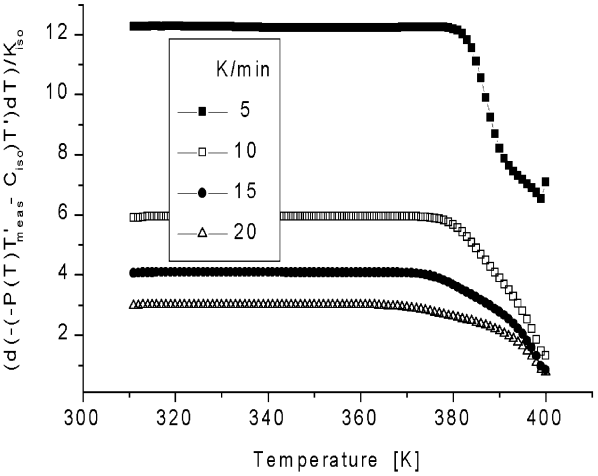

Fig. 5. Plot representing the temperature dependence of the sum of hypothetical coefficients $\tilde{A}_1$ and $\tilde{B}_1$ connected to the transient and athermal effects observed during non-isothermal crystallization of *i*-polypropylene at different cooling rates.

cooling rate, in the region of high temperatures showing an increase with a decrease of temperature followed by saturation in the region of low temperatures.

This dependence may result from the temperature dependence of the relaxation time, $\tau(T)$, which can be expected to increase with a decrease of temperature. As indicated by Ziabicki [26,27], the temperature dependent coefficients A_1 and B_1 can be expressed through thermodynamic characteristics of crystallization and the relaxation time τ.

The corresponding relationships can be written:

$$A_1 = {A_1}' \times \tau \tag{18a}$$

and

$$B_1 = {B_1}' \times \tau \tag{18b}$$

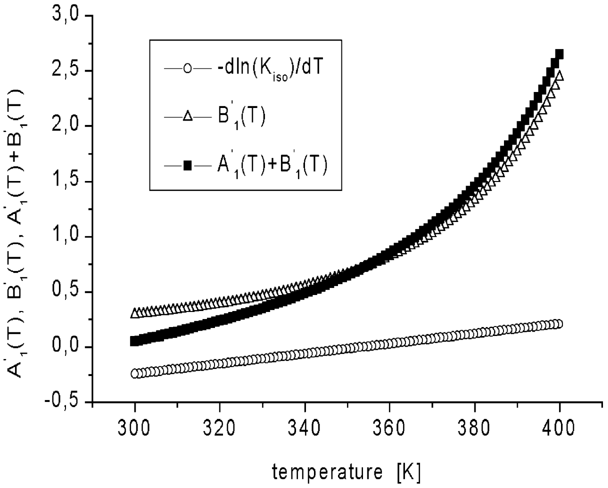

Fig. 6. Theoretical values of coefficients A_1/τ and B_1/τ and their sum as functions of temperature.

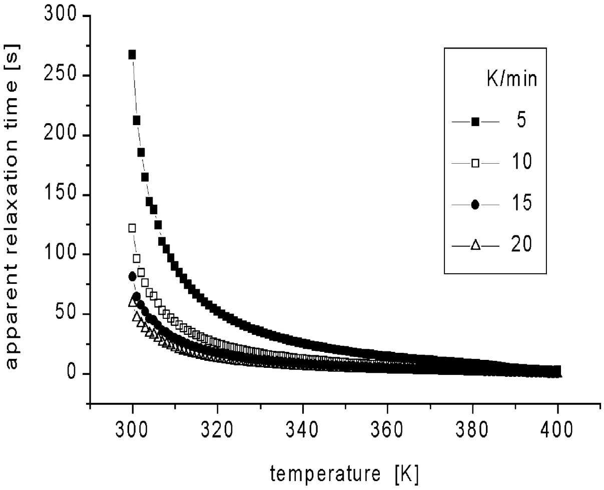

Fig. 7. The apparent relaxation time, τ_{app}, as a function of temperature for various cooling rates.

Comparison of numerical values of a function ${A_1}' + {B_1}'$ estimated on the basis of physical characteristics and equations given by Ziabicki [26] with experimentally determined coefficients $\tilde{A}_1$ and $\tilde{B}_1$, enables the estimation of relaxation time. The results of calculations performed with the use of Eqs. (5), (6), (14) and (18), with numerical values $\sigma = 23\ \mathrm{erg/cm}^2$, $T_{\mathrm{m}} = 481.2$ K, and $\Delta h = 1.4 \times 10^9\ \mathrm{erg/cm}^3$ are presented in Fig. 6.

Finally the apparent relaxation time is given in Fig. 7. The temperature dependence of the apparent relaxation time shows a realistic shape and provides a satisfactory explanation for the shape of crystallization rate dependence on temperature and cooling rate. It however shows an unexpected dependence of relaxation time on the cooling rate, which most probably still reflects the effect of athermal nucleation. This fact may indicate either that it is incorrect to assume that steady-state crystallization rate can be represented by a single function independent of cooling rate or that coefficients A_1 and B_1, being first terms of expansion are not sufficient to offer complete quantitative description of the observed dependencies.

5. Conclusions

The temperature dependence of the apparent relaxation time for transient crystallization, determined directly from non-isothermal crystallization, shows realistic values, being much smaller than those estimated in the indirect way [24]. The values for the first time obtained in direct way are slightly affected by relatively small contribution of athermal effects, that probably could be taken into account by further terms of the expansion. The substantial increase of relaxation time with the decreasing temperature appears to be the main factor causing a temperature dependent reduction of crystallization rate in the non-isothermal, continuous cooling processes with respect to that occurring in the isothermal ones.

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