

Method for Induction Time Determination Using Data Obtained From Isothermal Crystallization Experiment Monitored by DSC

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ABSTRACT: Previously introduced method for transforming kinetic function expression was applied on the differential form of isothermal Johnson–Mehl–Avrami (JMA) nucleation and growth equation, to determine the duration of the induction period, τ . The assisting function $\varphi = t^m$ was used to obtain a new equation, which enables determination of the induction time, τ , along with the Avrami parameter, n . The procedure was tested using a developed computer program on simulated data, experimental poly(ethylene-terephthalate) (PET) cold crystallization data, and poly(ester-ure-

thane) polycaprolactone-diol polymer (PEU) crystallization data obtained from literature. The test results show the validity of developed equations and their applicability for the determination of kinetic parameters, particularly the induction time. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2454–2458, 2004

Key words: calculations; crystallization; differential scanning calorimetry (DSC); induction time; JMA equation

INTRODUCTION

Differential scanning calorimetry (DSC) is used to investigate the reaction kinetics of a broad range of solid-state processes. The two basic approaches according to the experimental conditions are isothermal and nonisothermal. In isothermal experiments, the sample is quickly brought to the desired constant temperature, and the heat flow of the system is monitored as a function of time. In the classical approach, the DSC crystallization peak is transformed into a sigmoid crystallization curve, which represents the amount of heat released as a function of time, that is, the DSC peak area has to be integrated. The amount of the heat released at a given time, $\Delta H(t)$, is obtained by integrating the area enclosed by the baseline and the peak between the induction time, τ , (the crystallization starting point) and the elapsed time, t , (during the course of crystallization). The relative amount of heat is calculated by taking the ratio of $\Delta H(t)$ and the total heat of crystallization, ΔH , obtained by integration of the peak between τ and the reaction end point. Under the assumption that the evolution of crystallinity is linearly proportional to the heat released during the course of crystallization, the fraction transformed, α ,

also called relative crystallinity, can be calculated as a function of time through the following equation:

$$\alpha = \frac{\int_{\tau}^t \frac{dH}{dt} dt}{\int_{\tau}^{\infty} \frac{dH}{dt} dt} \quad (1)$$

To quantitatively describe the evolution of crystallinity under isothermal conditions, a number of kinetic models have been proposed. The Johnson–Mehl–Avrami (JMA) model^{1–4} is the most frequently used to describe nucleation and growth mechanism and it is based on the spherical growth of nuclei. This model is often applied to crystallization kinetics of various polymer materials.⁵ In the JMA model, the relative crystallinity as a function of time, $\alpha(t)$, relates to the crystallization time, t , according to the equation:

$$\alpha(t) = 1 - \exp[-(kt)^n] \quad (2)$$

where k is the crystallization rate constant (subject to the Arrhenius law), and n is the Avrami exponent. If the induction time, τ , is taken into account, then eq. (2) transforms into:^{6–7}

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$$\alpha(t) = 1 - \exp\{-[k(t - \tau)]^n\} \quad (3)$$

The differential form of JMA equation applicable to the isothermal process reads as:⁸⁻¹⁰

$$\frac{d\alpha}{dt} = nk^n t^{n-1} (1 - \alpha) \quad (4)$$

In DSC experiment, time elapsed between the thermal equilibrium point and the onset of the reaction is frequently observed. This elapsed time is called the induction time or incubation period of crystallization, and can be interpreted as a measure of time required for statistic processes to produce a nucleus of sufficient size for growth.^{11,12} With the induction time, the eq. (4) can be written:^{6,7}

$$\frac{d\alpha}{dt} = nk^n (t - \tau)^{n-1} (1 - \alpha) \quad (5)$$

This particular form of JMA equation is not well suited for computation since it combines both the fraction of noncrystallized material and the rate of reaction. To obtain (1- α), a numerical integration of experimental data is necessary and solving the eq. (5) becomes cumbersome.

The rate of the crystallization process can be directly obtained from the current values of the parameters fitted if the rate of the crystallization processes is expressed explicitly as a function of n, k , and τ . That is accomplished by substituting eq. (2) in eq. (4).

$$\frac{d\alpha}{dt} = nk^n t^{n-1} \exp[-(kt)^n] \quad (6)$$

The DSC curve can be fitted to the differential function eq. (6) (describing the JMA crystallization process) without previous integration.¹³ With the inclusion of induction time, the eq. (6) becomes:

$$\frac{d\alpha}{dt} = nk^n (t - \tau)^{n-1} \exp\{-[k(t - \tau)]^n\} \quad (7)$$

Evidently, whatever form of the function is chosen to calculate the kinetic parameters, determination of the induction time is an important element of kinetic analysis. For DSC investigations this parameter is usually set visually, as the point of the significant deflection from the baseline, which is a very subjective method. To define the induction time more accurately, the blank run has to be performed and subtracted from the isothermal crystallization scan. The start of the process is then taken as the intersection of the extrapolated baseline and the resulting exothermal curve.¹⁴ Foubert et al.¹⁵ gave more attention to this problem; in their work a calculation algorithm for determining the

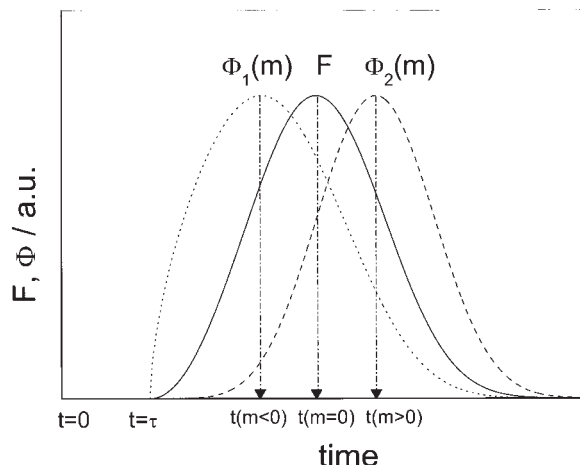


Figure 1 Kinetic function, F , (representing experimental data) and transformed functions $\Phi_1(m)$ and $\Phi_2(m)$. Maximum of the transformed function, $\Phi(m)$, occurs at different instants of time, $t(m)$, depending on the value of the parameter m . The fraction of noncrystallized material, $(1-\alpha(m))$, decreases in the course of time. Thus, as the parameter m increases, the fraction of noncrystallized material, proportional to the area under the kinetic curve, F , for times greater than particular $t(m)$, decreases.

start and end points of crystallization process was proposed.

In this work a previously introduced method of transforming kinetic function expression¹⁶ was applied to the differential forms of the isothermal JMA nucleation and growth model to determine the duration of the induction period, τ .

THE METHOD DEVELOPMENT

Recently, the utilization of assisting functions to transform the functions representing kinetic models has been introduced.¹⁶ The transformation is performed by multiplication of kinetic model function, F , with an assisting function, φ . In this manner the transformed function, Φ , is obtained.

$$\Phi = F\varphi \quad (8)$$

The differential forms of JMA equation, eqs. (5) and (7), were used as the kinetic model function, F . Beginning with eq. (5) and applying the assisting function $\varphi = t^m$, the obtained transformed function, Φ , equals:

$$\Phi(m) = Ft^m = nk^n (t - \tau)^{n-1} (1 - \alpha) t^m \quad (9)$$

The function $\Phi(m)$ has its maximum at $t = t(m)$, which for a given process depends only on m (k, n , and τ are constant) (Fig. 1). The value of the parameter m is chosen arbitrarily, thus yielding various transformed functions, $\Phi(m)$. It will be shown that a useful new relation is obtained between the parameter m , time of

the maximum of the transformed function, $t(m)$, reaction rate of the kinetic function at a time $t(m)$, $F(m)$, $(d\alpha/dt)|_{t=t(m)}$, fraction of noncrystallized material, $(1-\alpha(m))$, and the kinetic parameters, n , k , and τ .

For $m < 0$ the maximum of the transformed function ($\Phi_1(m)$ in Fig. 1) corresponds to a shorter time period compared with the maximum of the kinetic function, F , that is, $t(m < 0) < t(m = 0)$. Analogously, for $m > 0$ ($\Phi_2(m)$ in Fig. 1), the maximum of the transformed function corresponds to a greater time period than the maximum of the kinetic function, F , that is, $t(m > 0) > t(m = 0)$.

The time corresponding to the maximum of the transformed function, $\Phi(m)$, is obtained by equating its first time derivative to zero. For $d\Phi(m)/dt = 0$ one obtains:

$$\begin{aligned} \frac{d\Phi(m)}{dt} &= nk^n \left((n-1)(t-\tau)^{n-2}t^m(1-\alpha) \right. \\ &\quad \left. + (t-\tau)^{n-1} \left(-\frac{d\alpha}{dt} \right) t^m + (t-\tau)^{n-1}(1-\alpha)mt^{m-1} \right) = 0 \end{aligned} \quad (10)$$

The last equation can be rewritten as:

$$\begin{aligned} (n-1)(t-\tau)^{n-2}t^m \frac{A(m)}{C} - (t-\tau)^{n-1}t^m \frac{F(m)}{C} \\ + (t-\tau)^{n-1}mt^{m-1} \frac{A(m)}{C} = 0 \end{aligned} \quad (11)$$

where:

$$F(m) = C \left(\frac{d\alpha}{dt} \right) \Big|_{t=t(m)} \quad (12)$$

$$A(m) = \int_{t(m)}^{\infty} C \left(\frac{d\alpha}{dt} \right) dt = C(1-\alpha(m)) \quad (13)$$

The significance of $A(m)$ and $F(m)$ is illustrated in Figure 2.

C is proportionality constant dependent on the DSC instrument, and hence it does not influence the position of the peak of the transformed function $\Phi(m)$.

$$\begin{aligned} C^{-1}(t(m)-\tau)^{n-2}t(m)^{m-1}[(n-1)t(m)A(m) \\ - (t(m)-\tau)t(m)F(m) + m(t(m)-\tau)A(m)] = 0 \end{aligned} \quad (14)$$

For a particular value of m and $t > \tau$, it follows:

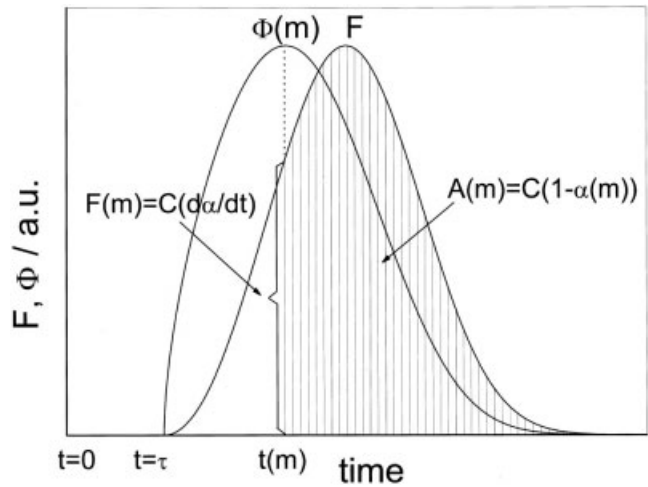


Figure 2 The functions F and $\Phi(m)$ versus time. The transformed kinetic function, $\Phi(m)$, has maximum at time $t = t(m)$. At the same time, $t(m)$, the rate of the reaction, $(d\alpha/dayt)$, is proportional to the value of the kinetic function, F , that is, its value equals $F(m) = C(d\alpha/dt)|_{t=t(m)}$. The fraction of noncrystallized material, $(1-\alpha(m))$, at the time of the maximum of the transformed kinetic function, $t(m)$, is proportional to the $A(m) = C(1-\alpha(m))$ (hatched area). Constant C is dependent on the experimental conditions and instrument setup.

$$\begin{aligned} n[t(m)A(m)] + \tau[F(m)t(m) - mA(m)] = F(m)t^2(m) \\ - A(m)t(m)(m-1) \end{aligned} \quad (15)$$

Eq. (15) is of the form $Z = nX + \tau Y$ and can be used to determine the parameters n and τ from a least squares fit through the origin. So, for the selected set of values of m , $t(m)$, $F(m)$, and $A(m)$, are obtained and n and τ are calculated by the least squares fit procedure.

Once the values of the kinetic parameters n and τ are known, the value of the reaction rate parameter k remains to be determined.

With that aim, eq. (5) is rewritten as:

$$\frac{\left(\frac{d\alpha}{dt} \right)}{n(1-\alpha)} = k^n(t-\tau)^{n-1} \quad (16)$$

and by introducing the notation from eqs. (12) and (13), after taking the n -th root the following is obtained:

$$\left(\frac{F(m)}{nA(m)} \right)^{1/n} = k(t(m)-\tau)^{(n-1)/n} \quad (17)$$

Eq. (17) is of the form $Y = kX$, where $Y = (F(m)/nA(m))^{1/n}$, $X = (t(m)-\tau)^{(n-1)/n}$, and k is obtained as a slope of the best line fit through the origin.

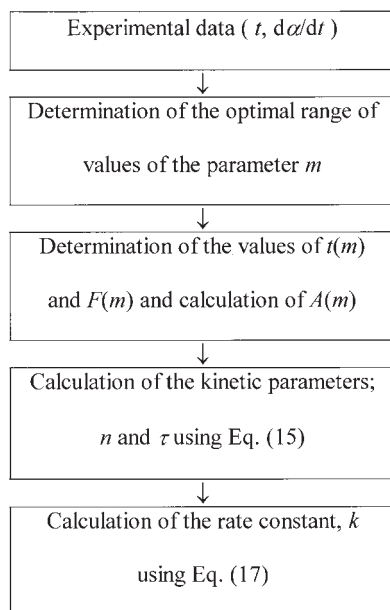


Figure 3 Schematic representation of the algorithm steps used for the calculation of the kinetic parameters τ , n , and k of the isothermal JMA process from the experimental data obtained in DSC experiment.

TESTING OF THE DERIVED MODEL

The computer program has been written in C++, which enables the calculation of the kinetic parameters (τ , n , and k) from the experimental isothermal DSC data of the nucleation and growth processes. The copy of the program can be obtained upon request from the authors. However, the algorithm can be easily programmed in a spreadsheet.

The flowchart of the program is given in Figure 3. The program starts with the determination of the range of the optimal values of the parameter m (in that range, DSC signal is equal to at least 10% of the maximum signal). Thus, 30 points are selected from the experimental data, covering the optimal range of values for the parameter m (shown as crosses in Fig. 4), and from that set of data (m , $t(m)$, $F(m)$, and $A(m)$), the values of the kinetic parameters n and τ are calculated according to eq. (15). The rate constant of the crystallization, k , is determined according to eq. (17). Higher data acquisition rate (greater number of data points) enables better selection of the values of $F(m)$ and $A(m)$ for a particular value of m .

The procedure has been tested on the model system ($n = 3$, $k = 0.00465 \text{ s}^{-1}$, $\tau = 100 \text{ s}$), on the literature data for the crystallization of nontoxic biodegradable polymer (PEU) of Bogdanov et al. (sample P4–36 at 30°C),¹⁷ and on the experimental data for poly(ethylene-terephthalate) (PET) cold crystallization at 105°C . A Netzsch differential scanning calorimeter, DSC 200, aluminum pan for PET specimen encapsulation, an empty pan as the reference, and liquid nitrogen as a

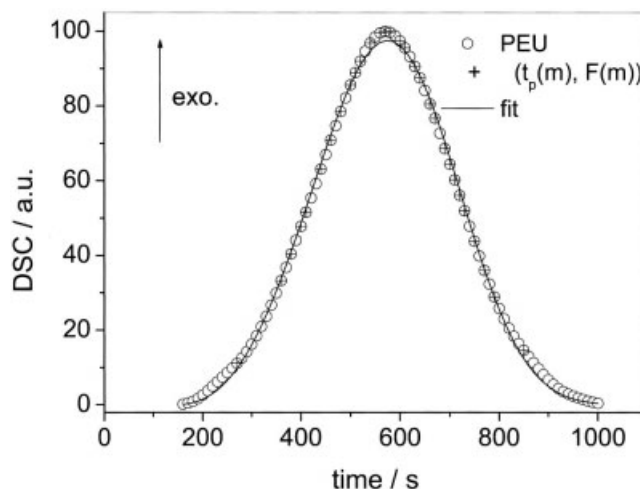


Figure 4 The DSC crystallization curve of poly(ester-urethane) polycaprolactone-diol polymer (PEU) at 30°C .¹⁷ Circles represent experimental data. The 30 points selected to cover the optimal range of the value of the parameter m ($t(m)$, $F(m)$) are shown as crosses. The fit of the isothermal JMA eq. (7) using the values of the calculated kinetic parameters n , k , and τ is shown as line.

coolant were used. The sample was heated to 300°C in inert nitrogen atmosphere to melt all crystallinity, rapidly cooled to room temperature to trap the material in amorphous state, and then heated to the dwell temperature to evaluate the kinetics of crystallization.

The kinetic parameters τ , n , and k obtained by applying the method to the simulated, experimental, and literature data are presented in Table I. Range of the values of the parameter m used in the calculations are also given. Standard deviation of the isothermal JMA fit (eq. 7) obtained using calculated values of the kinetic parameters is listed in the last row of the table.

The results in Table I show that the application of the proposed method on simulated DSC curve results in excellent concordance of simulated and calculated data. The same procedure was successfully applied on PET and PEU isothermal crystallization data and the latter is shown in Figure 4. The goodness of the fit on experimental data is illustrated by Figure 4.

TABLE I
Kinetic Parameters Obtained by the Method Proposed in This Work for the Model System, Experimental Data, and Literature Data

	Model System	Experimental Data (PET)	Literature Data (PEU) ¹⁷
τ/s	100.1	42.6	135.9
n	3.00	2.09	3.47
k/s^{-1}	0.00464	0.00335	0.00206
m	$-7 \leq m \leq 10$	$-3 \leq m \leq 5$	$-3 \leq m \leq 10$
<i>st. dev.</i>	0.230	2.295	1.832

Using the proposed method, the induction times for crystallization of PET and PEU polymer materials were determined.

Our method enables the determination of Avrami exponent and rate constant as well, but once the induction time is known, these parameters can be calculated in the usual way, from the logarithmic form of eq. (3).

Although this method uses only the extreme of the transformed function $\Phi(m)$, the large part of the experimental DSC curve is used in the calculation of the kinetic parameters τ , n , and k (point selection is dependent on the value of the parameter m (Fig. 1)).

When analyzing the experimental data, one should bear in mind that the points corresponding to the smallest and the largest values of the parameter m (at the beginning and the end of the experimental DSC curve) have lower signal to noise ratio.

CONCLUSION

Previously developed method of transforming kinetic function expression was applied on differential forms of JMA model to determine the duration of the induction period, τ . The equations were developed for processing of experimental data and calculation of the kinetic parameters according to the isothermal JMA equation, namely, induction time, τ , Avrami parameter, n , and rate constant, k . The testing showed that equations developed are valid and that it is possible to use them for determination of kinetic parameters, particularly induction time.

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References

1. Johnson, W. A.; Mehl, R. F. *Trans Am Inst Min Metall Engrs* 1939, 135, 416.
2. Avrami, M. *J Chem Phys* 1939, 7, 1103.
3. Avrami, M. *J Chem Phys* 1940, 8, 212.
4. Avrami, M. *J Chem Phys* 1941, 9, 177.
5. He, J. D.; Cheung, M. K.; Yang, M. S.; Qi, Z. *J Appl Polym Sci* 2003, 89, 3404.
6. Thompson, C. V.; Greer, A. L.; Spaepen, F. *Acta Metall* 1983, 31, 1883.
7. Kelton, K. F. *J Non-Cryst Solids* 1993, 163, 283.
8. Burke, J. *The Kinetics of Phase Transformations in Metals*; Pergamon: Oxford, 1965.
9. Marotta, A.; Buri, A.; Pernice, P. *Phys Chem Glass* 1980, 21, 94.
10. Markworth, A. J.; Glasser, M. L. *J Appl Phys* 1983, 54, 3502.
11. Luborsky, F. E. *Mater Sci Eng* 1977, 28, 139.
12. Altounian, Z.; Guo-Hua, T.; Stroem-Olsen, J. O.; Muir, W. B. *Phys Rev B* 1981, 24, 505.
13. Kurajica, S.; Bezjak, A.; Tkalcec, E. *Thermochimica Acta* 2000, 360, 63.
14. Siracusa, V.; Finelli, L.; Lotti, N.; Munari, A. *J Appl Polym Sci* 2003, 90, 2003.
15. Foubert, I.; Vanrolleghem, P. A.; Dewettinck, K. *Thermochimica Acta* 2003, 400, 131.
16. Bezjak, A.; Kurajica, S.; Šipušić, J. *Thermochimica Acta* 2002, 386, 81.
17. Bogdanov, B.; Toncheva, V.; Schacht, E.; Finelli, L.; Sarti, B.; Scandola, M. *Polymer* 1999, 40, 3171.