

ON A DIFFERENTIAL EQUATION FOR KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION

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ABSTRACT

A new differential equation was derived from the modified first-order kinetic model to describe the polymer crystallization processes. The crystallization experiments were carried out by means of DSC. Poly (ethylene terephthalate) resins were selected as the samples containing different catalysts. The relationships between the parameters obtained from the known Avrami equation and from one in the present paper were discussed. A method for applying the equation to determine the kinetic parameters from a constant heating and a constant cooling curve was proposed.

INTRODUCTION

Most of the melt-spinning of chemical fibers and the processing of plastics were carried out under non-isothermal condition, and thus it is of important significance to investigate the kinetics of non-isothermal crystallization of polymers in optimizing the technological processes of polymers.

In any heat transfer problem, the progress of crystallization is coupled with the energy equation concerned with heat conduction. It is necessary to find a differential form of the kinetic expressions which could dovetail into the differential heat transfer equation.

In determining the parameters characterizing kinetics of the polymer crystallization, the advantages of the method for the non-isothermal crystallization include that an abundance of information can be obtained, short time may be required, and the experiment is easier than the isothermal one.

So one has been paying attention to the study on the kinetics of the non-isothermal crystallization. The Avrami equation is normally used to describe the kinetics of the isothermal crystallization of polymers^[1] and extended to the non-isothermal situation^[2-4]. The Avrami equation is written in the integral form and it is not convenient for use under the non-isothermal condition where a differential form of the equation is concerned with the heat-transfer equation. So one has to attempt to develop the differential equation applicable to the non-isothermal courses. Ziabicki^[5] was the first to apply the first-order kinetic equation to the non-isothermal crystallization processes. Strictly speaking, the first-order kinetic model corresponds to one-dimensional growth of predetermined nuclei and does not coincide with the results attained from the Avrami equation when the crystallization mechanism of the samples is not like ^[6]. Lee and Kim^[7] derived a differential equation which could be used only in the case of the

nonisothermal crystallization of three-dimensional growth of predetermined nuclei. An equation of the autocatalytic type was proposed by Malkin and cooperators^[8-10], who named the equation "Macrokinetic equation". Recently, Malkin pointed out that the equation obtained by Lee and Kim was completely equivalent to one proposed by them^[11]. As the actual crystallization processes might be very complex, it is necessary to develop a new non-isothermal kinetic equation that is suitable for the different nucleation and crystal growth mechanism.

In this paper, a new kinetic equation for describing the non-isothermal crystallization was proposed. The derived equation was compared with the known Avrami equation and was used to determine the kinetic parameters from a constant heating and a constant cooling curve.

THEORY

Because the rate of crystallization depends on the existing surface area of crystallites, the more the crystal surface area the higher the rate of crystallization is. The Avrami equation and the modified Avrami equation could be derived from the modified first-order kinetic model^[12]. Evidently, it seems to be reasonable by using the modified first-order kinetic model to describe the crystallization of polymers. The model reads

$$\frac{dC_r}{dt} = SK'(1 - C_r) \quad (1)$$

where C_r is the relative crystallinity at time t ; S the total surface area of the crystallites on which the macromolecular segments can be deposited and K' a constant at a given temperature.

In case that the nuclei are pre-determined, i. e., all the nuclei are formed simultaneously and grow in three dimensions into the spherulites, the relationship between the total surface area ($S = 4\pi N_0 r^2$, where r is the radius of a spherulite) and volume of the spherulites ($V = \frac{4}{3} \pi N_0 r^3$) can be expressed by

$$S = 4\pi N_0 \left(\frac{3V}{4\pi N_0} \right)^{2/3} \quad (2)$$

where N_0 is the number of nuclei per unit mass. In the system per unit mass, $C_r = m_c/X_c$ (m_c the mass of the crystalline entities) and thus the relation between the total volume and the relative crystallinity can be written as

$$V = X_c C_r / \rho_c \quad (3)$$

where X_c is the equilibrium crystallinity; ρ_c the density of crystalline entities (e.g., the rods, disks or spheres). Inserting equation (3) into (2), one obtains

$$S = 4\pi N_0 \left(\frac{3X_c}{4\pi N_0 \rho_c} \right)^{2/3} \cdot C_r^{2/3} \quad (4)$$

With disk-shaped entities, the surface area on which the crystallization can take place depends only on the disk's perimeter and thickness (d_0), and the relationship between the surface area and the relative crystallinity is given by

$$S = 2(\pi d_0 N_0 X_c / \rho_c)^{1/2} \cdot C_r^{1/2} \quad (5)$$

For the rodlike entities, the surface area, i.e., the cross section, on which

the segments can be crystallizable, remains constant, thus

$$S = N_0 S' \quad (6)$$

where S' is the surface area of the cross section per rodlike entity.

With the sporadic nucleation, the time dependence of the total volume of the entities can be expressed as

$$V = \int_0^t \frac{dN}{d\tau} v(t, \tau) d\tau \quad (7)$$

where $v(t, \tau)$ is the volume at time t of a growing entity formed at time τ ; $dN/d\tau$ is the nucleation rate which can be assumed to be a function of temperature^[9]

$$\frac{dN}{dt} = I(T) \quad (8)$$

If an entity forms at time τ and grows thereafter isotropically in three dimensions into a sphere, then

$$v(t, \tau) = \frac{4}{3} \pi \left[\int_{\tau}^t G(\mu) d\mu \right]^3 \quad (9)$$

where $G(\mu)$ is a linear growth rate in time μ . Inserting equations (8) and (9) in to (7), one obtains

$$V = \frac{4}{3} \pi \int_0^t I \left[\int_{\tau}^t G(\mu) d\mu \right]^3 d\tau \quad (10)$$

For the convenience of analysis, the following transformation was introduced

$$r(t) = \int_0^t G(\tau) d\tau \quad (11)$$

then

$$dr = G(\tau) d\tau \quad (12)$$

Taking into account relationships (11) and (12), equation (10) becomes

$$V = \frac{4}{3} \pi \int_0^r \frac{I}{G} (r - r')^3 dr' \quad (13)$$

Assume that I/G is independent of temperature and let $I/G = k$, equation (13) can be integrated and leads to

$$V = \frac{1}{3} \pi k \cdot r^4 \quad (14)$$

The total surface area of the entities on which crystallization run can be expressed as

$$S = \int_0^t I s(t, \tau) d\tau \quad (15)$$

where $s(t, \tau)$ is the surface area at time t of a growing entity appearing at time τ . With spheres, the $s(t, \tau)$ is described as

$$s(t, \tau) = 4\pi \left[\int_{\tau}^t G(\mu) d\mu \right]^2 \quad (16)$$

Taking equations (11), (12), and (16) into account, equation (15) yields

$$\begin{aligned} S &= 4\pi \frac{I}{G} \int_0^r (r-r')^2 dr' \\ &= \frac{4}{3} \pi k \cdot r^3 \end{aligned} \tag{17}$$

Combining equations (3) and (14) with (17), one obtains

$$S = \frac{4}{3} \pi k \left(\frac{3X_c}{\pi \rho_c k} \right)^{3/4} \cdot C_r^{3/4} \tag{18}$$

With disked entities , the total volume is

$$\begin{aligned} V &= \pi d_0 \int_0^r \frac{I}{G} (r-r')^2 dr' \\ &= \frac{1}{3} \pi d_0 k \cdot r^3 \end{aligned} \tag{19}$$

The growing area is

$$S = 2\pi d_0 k \int_0^r (r-r') dr' = \pi d_0 k \cdot r^2 \tag{20}$$

Therefore

$$S = \pi d_0 k \left(\frac{3X_c}{\pi d_0 k \rho_c} \right)^{2/3} \cdot C_r^{2/3} \tag{21}$$

With rod shaped entities, one obtains

$$V = S' k \int_0^r (r-r') dr' = \frac{1}{2} S' k \cdot r^2 \tag{22}$$

$$S = S' k \cdot r \tag{23}$$

The relationship between the growing area and the relative crystallinity reads

$$S = (2X_c S' k / \rho_c)^{1/2} \cdot C_r^{1/2} \tag{24}$$

If these expressions for *S* are inserted into equation (1), the equation of the general form is obtained

$$\frac{dC_r}{dt} = K C_r^m (1 - C_r) \tag{25}$$

where *K* refers to the rate constant of crystallization. The physical significances of the exponent *m* are listed in Table 1. The values of the Avrami exponent *n* are also listed in Table 1 in order to compare it with *m*.

Table 1 Comparison of the constants *m* and *n*

Shape	Instantaneous		Sporadic	
	<i>m</i>	<i>n</i>	<i>m</i>	<i>n</i>
Sphere	2/3	3	3/4	4
Disk	1/2	2	2/3	3
Rod	0	1	1/2	2

The equation derived by us is the differential equation for describing kinetics of non-isothermal crystallization.

EXPERIMENTAL

The samples used in this study were poly (ethylene terephthalate) with different catalysts^[13]. A Perkin Elmer DSC-2c was used for the determination of crystallization processes: nitrogen atmosphere; melted for 10 minutes at 550K; the isothermal crystallization at 495K; the cooling and the heating curve at the rate of 5K/min.

RESULTS AND DISCUSSION

1. Comparison with the Avrami equation

The kinetics of the isothermal crystallization are normally described according to the Avrami equation^[1]

$$1 - C_r = \exp(-Zt^n) \quad (26)$$

where Z is the composite crystallization rate constant, t the time, and n the Avrami exponent. The numerical value of n depends on certain nucleation and growth mechanisms, as summed in Table 1.

The half life of crystallization is given by

$$t_{\frac{1}{2}} = \left(\frac{\ln 2}{Z} \right)^{1/n} \quad (27)$$

Comparing the values of m with n , as seen in Table 1, the relationship between m and n can be derived, i.e.

$$m = \frac{n-1}{n} \quad (28)$$

Under isothermal conditions, taking the derivative of equation (26) with respect to time leads to

$$\frac{dC_r}{dt} = Zn t^{n-1} (1 - C_r) \quad (29)$$

Combining equation (29) with (26) results in

$$\frac{dC_r}{dt} = nZ^{1/n} [-\ln(1 - C_r)]^{(n-1)/n} (1 - C_r) \quad (30)$$

Because that $(n-1)/n = m$ and $-\ln(1 - C_r) \approx C_r$ at lower crystallinity, comparing equation (25) with (30), one gets

$$K \approx nZ^{1/n} \quad (31)$$

According to the Avrami equation, both n and Z can be obtained by plotting $\ln[-\ln(1 - C_r)]$ versus $\ln t$ under isothermal conditions, the slope being n and the

intercept $\ln Z$. From equation (25) a plot of $\ln\left(\frac{1}{1 - C_r} \frac{dC_r}{dt}\right)$ against $\ln C_r$

should yield a straight line with a slope of m and an intercept of $\ln K$. m is the parameter characterizing the mechanisms of crystallization and K the parameter describing the rate of crystallization. The plots from the Avrami equation and from equation (25) were shown in Figure 1 and 2 respectively. The parameters given by Figure 1 and 2 were listed in Table 2. From knowledge of the values of K and m , the values of n , Z , and $t_{\frac{1}{2}}$ can be estimated by equations (28), (31), and (27) respectively and were also listed in Table 2. It can be seen that the

Table 2 Comparison of parameters characterizing the crystallization kinetics of poly(ethylene terephthalate)

No.	Method of the present paper					The Avrami method		
	<i>m</i>	<i>K</i> (min ⁻¹)	<i>n</i>	<i>Z</i> (min ^{-<i>n</i>})	<i>t</i> ^{1/2} (min)	<i>n</i>	<i>Z</i> (min ^{-<i>n</i>})	<i>t</i> ^{1/2} (min)
1	0.628	0.159	2.69	4.99 × 10 ⁻⁴	14.8	2.69	4.31 × 10 ⁻⁴	15.6
2	0.698	0.432	3.31	1.18 × 10 ⁻³	6.86	2.85	3.12 × 10 ⁻³	6.66
3	0.669	0.625	3.02	8.56 × 10 ⁻³	4.28	2.54	2.02 × 10 ⁻²	4.02
4	0.725	3.56	3.64	9.26 × 10 ⁻¹	0.92	3.06	7.26 × 10 ⁻¹	0.99

results obtained from equation (25) are approximately in agreement with those from the Avrami equation.

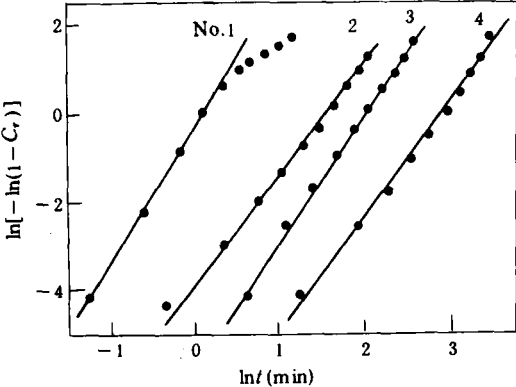


Fig. 1 The Avrami analysis of isotherms of the crystallization of poly (ethylene terephthalate)

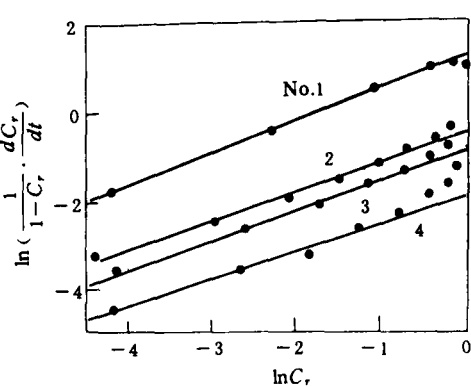


Fig. 2 The plots of $\ln\left(\frac{1}{1 - C_r} \cdot \frac{dC_r}{dt}\right)$ versus $\ln C_r$, the crystallization of poly (ethylene terephthalate)

2. An example for applying the differential equation to the non-isothermal situation

One method for determination of the parameters characterizing crystallization kinetics was proposed by using DSC curves with a constant heating and a constant cooling rate in terms of the differential equation. Under non-isothermal conditions, equation (25) can be written in the following form

$$\beta \frac{dC_r}{dT} = K C_r^m (1 - C_r) \tag{32}$$

where β is the rate of heating or cooling. If the temperature dependence of the rate constant of crystallization K is expressed by^[14]

$$K = K_0 \exp \left(- \frac{Ed}{RT} - \frac{\psi T_m^{02}}{T^2 (T_m^0 - T)} \right) \tag{33}$$

then, from equations (32) and (33), one obtains

$$\ln \left(\frac{\beta}{1 - C_r} \cdot \frac{dC_r}{dT} \right) = \ln K_0 - \frac{Ed}{RT} - \frac{\psi T_m^{02}}{T^2 (T_m^0 - T)} + m \ln (C_r) \tag{34}$$

where K_0 approaches to a constant; Ed stands for the activation energy for

transport; ψ the nucleation parameter. T_m^0 the equilibrium melting temperature; R the gas constant. Let $y = \ln ((\beta/(1 - C_r)) \cdot (dC_r/dT))$, $x_1 = 1/T$, $x_2 = T_m^{02}/T^2(T_m^0 - T)$, and $x_3 = \ln(C_r)$, equation (34) becomes

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 \tag{35}$$

where $b_0 = \ln K_0$; $b_1 = -Ed/R$; $b_2 = -\psi$; $b_3 = m$. Equation (35) is the multiple linear model. The coefficients b_i ($i = 0, 1, 2$, and 3) can be obtained by using a linear least squares procedure^[14]. In case $T_m^0 = 583\text{K}$ ^[14], then $K_0 = 8.88 \times 10^{-10}\text{min}^{-1}$; $Ed = 47.3\text{KJ/mol}$; $\psi = 888.3\text{K}$; $= 0.666$. (In order to derive the reliable parameters, the relative crystallinity selected to fit the curves had better be lower than 65%). Inserting these parameters into equation (33), the values of K can be calculated at various temperatures, as shown in Figure 3. The solid lines stand for the temperature range in which the experiment data such as dC_r/dT and C_r can be acquired. The dotted lines were calculated from the parameters derived by the least squares procedure.

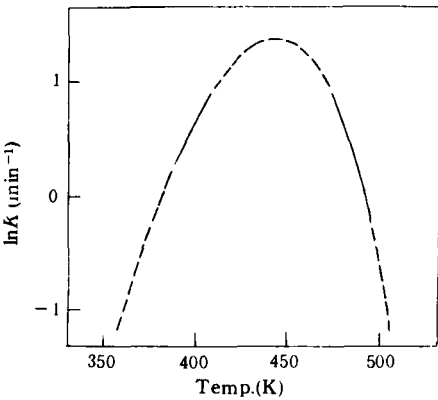


Fig. 3 The temperature dependence of the rate constant K ; the sample used is No.1

CONCLUSION

A new differential equation for describing the kinetics of non-isothermal crystallization was derived from the modified first-order kinetic model

$$\frac{dC_r}{dt} = KC_r^m (1 - C_r)$$

The relationship between m and the Avrami exponent n follows

$$m = \frac{n-1}{n}$$

The relationship between the rate constant K and the composite rate constant Z can be approximately expressed as

$$K \approx nZ^{1/n}$$

The parameters such as the activation energy for transport, the nucleation parameter, and the exponent m can be obtained, and then the rate constant K can be calculated in terms of the present method.

Keywords:

Non-isothermal crystallization; Crystallization kinetics; Polymer; Differential scanning calorimetry (DSC).

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