A multivariate linear regression method based on an improved rate equation to determine parameters of nonisothermal crystallization kinetics

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ABSTRACT

An improved rate equation was proposed to investigate nonisothermal crystallization kinetics. The reaction model, activation energy and pre-exponential factor were determined by using the multivariate linear regression method. A particular form of the effective activation energy was derived from the improved rate equation, and experimental data reported in previous studies were used to validate the reliability of the proposed rate equation. Results indicate that the values of effective activation energy obtained from the improved rate equation are similar to those obtained from the isoconversional method. When the improved rate equation is used to fit the crystallization rates under different cooling or heating rates simultaneously, the correlation coefficient is between 0.982 and 0.998, which indicates that the proposed rate equation is capable of describing the variation of the crystallization rates during nonisothermal processes.

1. Introduction

Crystallization is a process that involves two steps known as nucleation and growth. The rates of the two steps could be studied by crystallization kinetics. The majority of kinetic methods used in thermal analysis consider the rate to be a function of two variables [1]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the relative crystallinity, $k(T)$ is the rate constant at temperature T, and $f(\alpha)$ is a function of α. The rate constant is commonly expressed as the Arrhenius equation:

$$k(T) = A\exp\left(\frac{-Ea}{RT}\right) \tag{2}$$

where A is the pre-exponential factor. Ea is the activation energy for crystallization. R is the universal gas constant, and T is absolute temperature. By using the general Sestak-Berggren model [2], Eq. (1) can also be expressed as:

$$\ln\frac{d\alpha}{dt} = lnA - \frac{Ea}{RT} + mln\alpha + nln(1-\alpha) + pln(-ln(1-\alpha)) \tag{3}$$

where the kinetic parameters A, Ea, m, n, p can be determined by using the fitting method. The crystallization kinetics during nonisothermal process could also be described by using single-step models, such as the Avrami equation and the Ozawa method [3–5]. However, for different

kinetic models, the form of the rate equation is different. When the relative crystallinity is described by the Avrami Equation, the crystallization rate is expressed as a product of a function of relative crystallinity and a function of time:

$$\frac{d\alpha}{dt} = n(1-\alpha)(-ln(1-\alpha))\frac{1}{t} \tag{4}$$

where n is the Avrami exponent which is dependent on the growth geometry of the crystals and on the type of nucleation [3]. When the Ozawa equation is used to determine the relative crystallinity, the crystallization rate relates to three variables including the relative crystallinity, the temperature and the cooling/heating rate [6,7]:

$$\frac{d\alpha}{dt} = (1-\alpha)\frac{d\gamma(T)}{dT}\beta^{1-n_0} \tag{5}$$

where $\gamma(T)$ is a cooling function and n_0 is the Ozawa exponent associated with nucleation and crystal growth mechanism. β is cooling rate or heating rate during nonisothermal process. It is difficult to convert Eq. (1) to Eq. (4) or Eq. (5). Therefore, the activation energy of nonisothermal crystallization process could not be obtained from the Avrami equation or the Ozawa equation. Based on the assumption of a first-order reaction, the Kissinger method is derived for determining the activation energy [8]. It is noted that the activation energy obtained from the Kissinger method is a constant value for any process, which indicates that the activation energy can only represent single-step kinetics.

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Due to the non-Arrhenius character of many processes, the rate equation expressed as Eq. (1) may not be appropriate for determining the crystallization rate of nonisothermal processes. An effective improvement for the rate equation is to assume that the single-step Eq. (1) is applicable only to a single extent of conversion [9]. In this case, at a constant extent of conversion, the reaction rate is only a function of temperature, which is known as the isoconversional principle [10]. Unlike the Kissinger method, the isoconversional method could be used to describe the variation of the effective activation energy $E\alpha$ during nonisothermal process [11,12]. Because the isoconversional method is capable of describing the kinetics of multi-step and non-Arrhenius processes, the activation energy obtained from this method is more reliable for estimating the activation energy than the Kissinger method [13]. When the isoconversional method is used to determine the value of $E\alpha$, the identification of reaction model is unnecessary [14], and a particular form of $E\alpha$ could not be obtained. However, by applying the Hoffman-Lauritzen theory, the temperature dependence of the effective activation energy could be investigated [12,13]. For nonisothermal crystallization process, the temperature at a given α varies with cooling rate. Thus, if the effective activation energy is considered as a function of temperature, the value of the effective activation energy at a given α is different under different cooling or heating rates. However, the value of $E\alpha$ obtained from the isoconversional method is a constant, which is not consistent with the effective activation energy obtained from the Hoffman-Lauritzen theory. Therefore, the temperature is not the only factor that could influence the effective activation energy, and further investigations are necessary to interpret the temperature dependence of the effective activation energy.

In this paper, an improved rate equation is proposed to simulate the variation of the crystallization rate during nonisothermal process, and the multivariate linear regression method is used to obtain the kinetic parameters, including the reaction model, the activation energy and the pre-exponential factor. A particular form of the $E\alpha$ is derived for studying the temperature dependence of the effective activation energy. Experimental data reported in previous studies are used to validate the reliability of the proposed equation. Besides, the value of the effective activation energy obtained from the improved rate equation is compared with the result obtained from the isoconversional method.

2. Theoretical background

In this section, a rate equation used to determine the crystallization rate of nonisothermal process is derived according to commonly used kinetic models. In order to describe the crystallization rate with a general equation, a two-variable function is constructed:

$$h(T, t) = k(T)(A \times t)^q \tag{6}$$

where $k(T)$ is the rate constant. q is a constant. According to Eq. (4), the crystallization rate derived from the Avrami equation could be considered as a product of a function of relative crystallinity and a function of time. For the Ozawa equation, the crystallization rate could be considered as a product of a function of relative crystallinity and a two-variable function of temperature and cooling rate, as shown in Eq. (5). For the isoconversional method used to calculate the effective activation energy, the crystallization rate for a whole process could be expressed as a product of a one-variable function of relative crystallinity and a two-variable function of temperature and relative crystallinity. Because the relative crystallinity could be considered as a two-variable function of time and temperature, the rate equations derived from the above three models could be expressed as an unified form:

$$\frac{d\alpha}{dt} = f(\alpha)g(T, t)h(T, t) \tag{7}$$

where $f(\alpha)$ is a function of α. $g(T,t)$ is a two-variable function of temperature and time. The different forms of $g(T,t)$ derived from the Avrami equation, the Ozawa model and the isoconversional method are

shown in Eqs. (8), (9) and (10), respectively.

$$g(T, t) = \frac{n}{t \times h(T, t)} \tag{8}$$

$$g(T, t) = \frac{d\gamma(T)}{dt} \left| \frac{T - T_0}{t} \right|^{-n_0} \frac{1}{h(T, t)} \tag{9}$$

$$g(T, t) = A\exp\left(\frac{-E_\alpha}{RT}\right)\frac{1}{h(T, t)} \tag{10}$$

The two-variable function $g(T,t)$ could be considered as a function of relative crystallinity when Eq. (11) is satisfied.

$$\begin{cases} \alpha(T_1, t_1) = \alpha(T_2, t_2) = \alpha(T_3, t_3)=\cdots=\alpha(T_i, t_j) = \cdots \\ g(T_1, t_1) = g(T_2, t_2) = g(T_3, t_3)=\cdots=g(T_i, t_j) = \cdots \end{cases} \tag{11}$$

In Eq. (11), temperature T_i corresponds to time t_j under a given temperature program. For experimental data under different cooling or heating rates, the temperature under a given α is different. If the values of $g(T_i,T_j)$ under these temperatures are the same, the value of $g(T_i,T_j)$ is unique under a given α. Thus, the two-variable function could be considered as a function of α, and the crystallization rate can be re-written as:

$$\frac{d\alpha}{dt} = F(\alpha)k(T)U(T) \tag{12}$$

where $F(\alpha)$ is a function of relative crystallinity. According to the general Sestak-Berggren model, the function $F(\alpha)$ is written as:

$$F(\alpha) = f(\alpha)g(T, t) = \alpha^m(1 - \alpha)^n(-ln(1 - \alpha))^p \tag{13}$$

The $U(t)$ is a function of time, as shown in Eq. (14).

$$U(t) = A^q t^q \tag{14}$$

By taking the natural logarithm of the crystallization rate, the equation used for the multivariate linear regression method is expressed as:

$$ln\frac{d\alpha}{dt} = mln\alpha + nln(1 - \alpha) + pln(-ln(1 - \alpha)) - \frac{Ea}{R}\frac{1}{T} + qlnt$$
$$+ (q + 1)lnA \tag{15}$$

The relative crystallinity α can be obtained according to the heat flux measured by the Differential Scanning Calorimetry (DSC), as shown in Eq. (16).

$$\alpha = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \tag{16}$$

The variables and parameters in Eq. (15) could be expressed as two matrices, as shown in Eq. (17) and Eq. (18).

$$\begin{bmatrix} ln\alpha \\ ln(1 - \alpha) \\ ln(-ln(1 - \alpha)) \\ -\frac{1}{RT} \\ lnt \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{bmatrix} \tag{17}$$

$$\begin{bmatrix} m \\ n \\ p \\ Ea \\ q \\ (q + 1)lnA \end{bmatrix} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \end{bmatrix} \tag{18}$$

The experimental data used for the fitting method are multiple data sets obtained under different cooling or heating rates. Thus, by minimizing the difference between the experimental data and calculated results, the parameters m, n, p, q, Ea, A could be obtained from Eq. (19).