polymer communications

Re-examination of a proposed method to obtain Avrami parameters directly from non-isothermal crystallization data

Jinan Cao
CSIRO Division of Coal & Energy Technology, PO Box 136, North Ryde, NSW 2113, Australia
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This communication is a theoretical re-examination of the method to obtain Avrami parameters directly from non-isothermal crystallization data proposed by Dutta.

(Keywords: crystallization; non-isothermal; Avrami parameters; PET)

Introduction

The crystallization kinetics of a polymer are important in the elucidation of the crystallization mechanism and have been studied extensively. However, in the recent article by Dutta[1] entitled 'Method to obtain Avrami parameters directly from non-isothermal crystallization data', some important aspects were disregarded. These aspects will be addressed below.

Methodology

As noted by Dutta, the Avrami equation and the crystallization rate equation [Dutta's equations (1) and (3)] are applicable only for an isothermal crystallization. The temperature dependence of the crystallization rate constant k is, in this case, a comparison of crystallization rates of different isothermal crystallization processes. The isokinetic assumption which suggests that a non-isothermal crystallization can be expressed as the superposition of a sequence of small isothermal crystallization steps, does not mean that a non-isothermal crystallization may be dealt with as an isothermal process even in the case of a linear temperature change[2,3]. Dutta's non-isothermal equation (7) was derived by combining the effect of temperature on the crystallization rate constant k and the isothermal crystallization rate $\dot{\alpha}$ in equation (3), then differentiating $\dot{\alpha}$ with respect to time t. This treatment ignored the physical meaning of the Avrami equation, indicating a methodological error.

This error becomes more obvious if it is noted mathematically that when equation (7) was derived from equation (3), $\mathrm{d}k/\mathrm{d}t = -k\beta E'/T^2$ was employed; on the other hand, $\mathrm{d}k/\mathrm{d}t = 0$ was adopted in the derivation of equation (3) from equation (1) since an isothermal crystallization has been assumed.

Pre-exponential factor

The incorrectness of the method proposed by Dutta may be further demonstrated if one realizes that a different pre-exponential factor A will be obtained following the method. When the condition $\mathrm{d}^2\alpha/\mathrm{d}t^2 = 0$ is satisfied, the crystallization rate reaches its maximum. Substituting Dutta's equation (7) into Dutta's equation (3) leads to:

$$A = \frac{\dot{\alpha}_\mathrm{p}(T_\mathrm{p} - T_0)}{(1 - \alpha_\mathrm{p})\beta} \frac{1}{\left(\dfrac{T_\mathrm{p} - T_0}{\beta}\right)^n} \exp\left(-\frac{E'}{T_\mathrm{p}}\right)\frac{1}{n} \tag{1}$$

where all the symbols have the same meanings as those used by Dutta.

If the method is correct, a consistent A would be anticipated. *Table 1* shows the values of A calculated according to the above equation as well as the peak temperatures T_p calculated from the numerical readings of Dutta's Figure 2. It can be seen that the variation in A is too large to be acceptable. A contradictory pre-exponential factor will necessarily lead to an erroneous rate constant.

Non-isothermal crystallization and crystallization rate constant

It is worth mentioning that instead of the Avrami equation, the following generalized equation should be used for a non-isothermal crystallization under the isokinetic assumption:

$$\alpha = 1 - \exp\left(-\left\{\int_0^t k[T(\tau)]^{1/n}\mathrm{d}\tau\right\}^n\right) \tag{2}$$

where τ denotes the time variable of the integrand, and other symbols have the same meanings as those used by Dutta.

The effect of temperature on the crystallization rate constant k of a polymer is complicated. Even when discussion is limited to the case of poly(ethylene

Table 1 Values of A calculated from equation (1)

$\beta(\mathrm{K\,min^{-1}})$	$\dfrac{T_0 - T_\mathrm{p}}{T_\mathrm{p}^2}(\mathrm{K^{-1}})$	$\dfrac{\dot{\alpha}_\mathrm{p}(T_\mathrm{p} - T_0)}{(1 - \alpha_\mathrm{p})\beta}$	T_p (K)	$A\,(\mathrm{min}^{-n})$
−2	0.000419	18.167	477.6	2.6×10^{-40}
−3	0.000436	18.905	474.8	4.2×10^{-40}
−5	0.000459	19.762	471.2	7.2×10^{-40}

$T_0 = 573.1$ K, $E' = 40022.4\ \mathrm{K^{-1}}$, $n = 2.42$

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terephthalate) (PET), the Arrhenius relationship fails to interpret why a slow crystallization is observed when a PET melt is cooled to close to its glass transition temperature. It is well known that the crystallization rate dependence on temperature can be represented by a bell-shaped curve. The crystallization half-time of Gaussian type is given by[3,4]:

$$\frac{1}{t_{1/2}} = \frac{1}{t^*_{1/2}} \exp\left[-\frac{4\ln 2 (T - T^*)^2}{D^2} \right] \tag{3}$$

where $t^*_{1/2}$ is the minimum half-time corresponding to the maximum crystallization rate constant at the temperature T^*, and D is the width at half-height of the Gaussian curve. This relationship is certainly incompatible with the Arrhenius equation.

References

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