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On the physical dimensions of the Avrami constant[☆]

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Abstract

In this note, some discrepancies in the utilization of the Avrami model adopted for the crystallization modelling of advanced semicrystalline thermoplastic matrices are pointed out. In particular, the correct representation of the kinetic constants as a function of the isothermal crystallization temperature is discussed. In fact, Avrami analysis of isothermal crystallization data leads to the computation of kinetic constants characterized by physical dimensions depending on the calculated Avrami index. The representation on a single plot of these kinetic constants is not formally correct, and therefore a modification of the Avrami expression must be adopted.

Keywords: Avrami; Constants; Crystallization; Isothermal; Model

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1. Introduction

The application of a macrokinetic approach to polymer crystallization is very useful for the analysis and design of shaping operations generally conducted under complex thermal conditions. In fact, processing of semicrystalline polymeric materials requires one or more cycles of heating and cooling involving melting and crystallization processes, which determine the development of the crystalline structure and the physical properties of the final product. These issues have been addressed in previous papers for advanced thermoplastic matrices, through the development and application

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of a kinetic model, based on isothermal and non-isothermal expressions of the Avrami equation [1], to the crystallization of poly(phenylene sulphide) (PPS), PPS matrix/carbon-fibre composite and new thermoplastic polyimide (TPI) [2–4]. The model, including the effects of nucleation, presents a simplified temperature dependence expression of the Avrami kinetic constant calculated from isothermal calorimetric crystallization experiments. In this note, the physical dimensions and the correct representation of the Avrami constant as a function of the isothermal crystallization temperature are discussed. The considerations presented here on the Avrami constant are referred to experimental data obtained by calorimetric analysis on new TPI, following procedures described elsewhere [4].

2. Calculation and representation of the Avrami constant

Many authors have been active in crystallization modelling of advanced semicrystalline thermoplastic matrices. However, some discrepancies in the utilization of the Avrami model and its constants are apparent. The Avrami model was originally written as

$$1 - X_r = \exp(-kt^n) \tag{1}$$

where X_r is the degree of crystallinity referred to its maximum value, t is the crystallization time, properly scaled by the induction time [2–4], and the exponent n and the kinetic constant k are the parameters characterizing the crystallization process. According to this expression, the physical dimension of k, s^{-n}, is dependent on the exponent n. The correct form of the Avrami equation, less frequently found in the literature, provides the correct physical dimensions of k (s^{-1})

$$1 - X_r = \exp[-(kt)^n] \tag{2}$$

The parameters of the Avrami isothermal crystallization model can be calculated from the analysis of isothermal experiments using the classical double-logarithm expression of Eq. (2)

$$\ln[-\ln(1 - X_r)] = n\ln(k) + n\ln(t) \tag{3}$$

However, the same analysis performed on Eq. (1) leads to a different value of k measured in (s^{-n})

$$\ln[-\ln(1 - X_r)] = \ln(k) + n\ln(t) \tag{4}$$

The values of n and k obtained for new TPI [4] applying Eqs. (3) and (4), are reported in Table 1 for cold and melt crystallization experiments. A slight dispersion in the individual values of the exponent n, obtained from different isothermal tests, can be observed and is normally considered as typical of this experimental approach.

The use of a mathematical model for the temperature dependence of k is a key factor for the simulation of non-isothermal crystallization processes [2–4]. Although the physical dimensions of k as obtained from Eq. 4 (s^{-n}) are dependent on the value of the Avrami exponent n, k is generally plotted as a function of the temperature, as shown in

Table 1
Parameters obtained from the Avrami analysis of experimental data

Temp./°C	n	$\ln(k/\mathrm{s}^{-n})$ from Eq. (4)	$\ln(k/\mathrm{s}^{-1})$ from Eq. (3)
290 (cold cryst.)	2.07	−14.45	−7.12
295 (cold cryst.)	2.09	−13.77	−6.59
300 (cold cryst.)	2.15	−13.20	−6.13
305 (cold cryst.)	2.01	−11.70	−5.82
310 (cold cryst.)	2.07	−11.60	−5.60
310 (melt cryst.)	2.05	−11.30	−5.51
315 (melt cryst.)	1.96	−10.77	−5.49
320 (melt cryst.)	2.03	−10.52	−5.18
330 (melt cryst.)	1.99	−10.30	−5.17
340 (melt cryst.)	2.10	−10.72	−5.11
350 (melt cryst.)	2.10	−11.70	−5.57
360 (melt cryst.)	2.13	−13.32	−6.25

Fig. 1 for our TPI results. Similar plots have been reported in the scientific literature for other semicrystalline polymers [2, 3, 5–10]. However, the plot of Fig. 1 is incorrect because kinetic constants can be compared on a single plot only if they have the same physical dimensions, i.e. the same n, or if they are calculated from Eqs. (2) and (3). This implies that the k values reported in Fig. 1 cannot be compared and processed for the verification of the temperature dependence of the kinetic process. However, when very small differences in n values are computed, the k values measured in (s^{-n}) may be successfully processed [2, 3] for the evaluation of their temperature dependence.

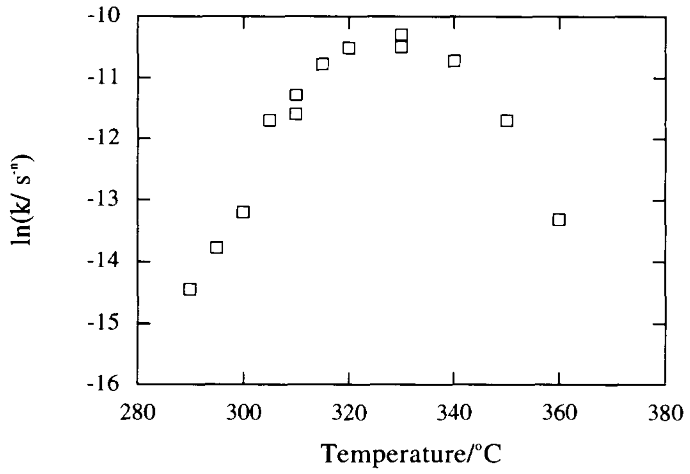

Fig. 1. Incorrect plot presenting the temperature dependence of the kinetic constants calculated from isothermal cold and melt crystallization performed by DSC according to Eq. (4). The physical dimensions of the plotted values of k are dependent on the Avrami exponent.

Only a few correct representations of Avrami constants, obtained following Eqs. (2) and (3), can be found in the polymer literature [4,11]. The k values, obtained from Eqs. (2) and (3) and reported in Fig. 2 are not affected by the experimental error on the Avrami exponent n. Moreover, these results display a lower scattering compared with the values of k shown in Fig. 1. Therefore any regression analysis of Fig. 2 results will provide improved correlation coefficients.

Figs. 1 and 2 show the characteristic bell-shaped curves representing the complex behaviour of the kinetic constants, k and k', as a function of the crystallization temperature T between the glass transition temperature T_g and, the theoretical melting point T_m^0. A simplified expression of the classical temperature dependence of k, previously proposed [2–4], can be adopted

$$k = k_0 \exp\left(-\frac{E_2}{R(T-T_g)}\right)\exp\left(-\frac{E_1}{R(T_m^0-T)}\right) \tag{5}$$

where E_1 and E_2 represent the activation energies accounting respectively for the counteracting effects of undercooling and diffusion, and k_0 is a kinetic constant. The values of k, obtained from isothermal DSC experiments performed at different temperatures, can now be used to compute the parameters of Eq. (5) by non-linear regression. A good agreement between model predictions and experimental values is observed in Fig. 2. The complete set of parameters of the kinetic model is reported in Table 2.

Finally it must be noted that the analysis of the non-isothermal crystallization has been traditionally approached starting from the classical Avrami model and obtaining integral or differential models with a temperature-dependent kinetic constant. In particular, Nakamura et al. [12] proposed the following integral expression obtained

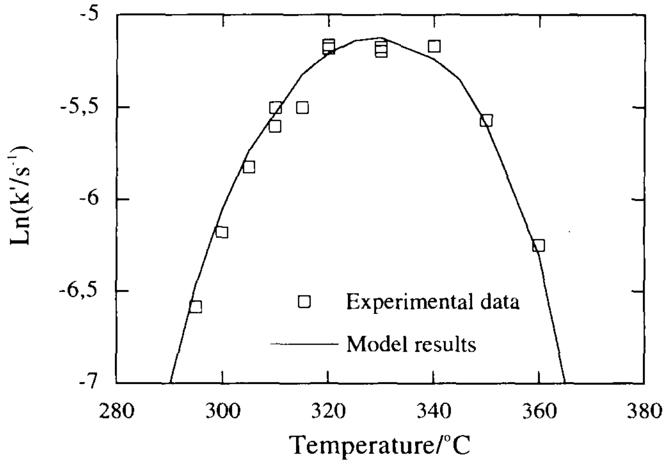

Fig. 2. Correct plot presenting the temperature dependence of the kinetic constants k calculated from each isothermal crystallization according to Eq. (3). Experimental data and Eq.(5) predictions.

Table 2
Parameters of the kinetic model (Eq. (5))

$\ln(k_0/\mathrm{s}^{-1}) = 0.33$	$(E_1/R)/\mathrm{K} = 176$	$(E_2/R)/\mathrm{K} = 235$
$T_g/°\mathrm{C} = 249$	$T_m^0/°\mathrm{C} = 399$	$\bar{n} = 2.06$

from the general Avrami theory

$$X_r(t) = 1 - \exp\left[-\left(\int_0^t k(T)\,\mathrm{d}t\right)^{\bar{n}}\right] \tag{6}$$

In Eq. (6), the physical dimensions of the kinetic constant k are s^{-1} and the proper model for its temperature dependence (like Eq. (5)) can be calculated by analysing the correct values of the kinetic constant obtained from the analysis of experimental data, following Eqs. (2) and (3).

3. Conclusions

The classical double-logarithm Avrami analysis of isothermal calorimetric crystallization data leads to the computation of kinetic constants characterized by physical dimensions depending on the calculated Avrami index. Therefore, the representation on a single plot of these kinetic constants is not formally correct. Scaling the physical dimensions of the kinetic constants to s^{-1} can be obtained when the correct form ofthe Avrami equation is adopted. The proposed procedures allowed a more correct definition of the temperature dependence model and a reduction of data scattering.

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