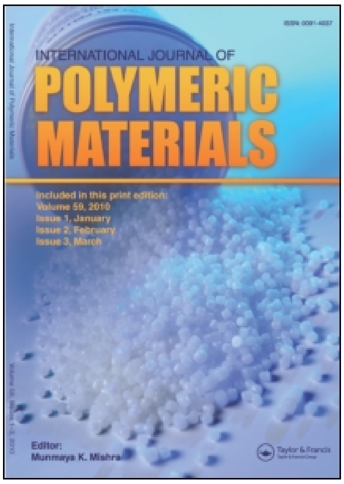

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Modeling Polymer Crystallization: T-CR-T Diagram Construction

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A description for solidification accounting for continuous cooling is presented. The analysis is based on the fact that nuclei have to be created prior to crystal growth. Furthermore, a modified isoconversional method is applied to perform the kinetic analysis of non-isothermal processes. The solidification process of different polymer materials: polypropylene – polyethylene and mixtures of polyethylene glycol with drug was here analyzed by means of differential scanning calorimetry.

Temperature-cooling rate-transformation diagrams were constructed and there was a good agreement between experimental data and the calculated T-CR-T curves.

Keywords: DSC; T-CR-T diagrams; Isoconversional method

1. INTRODUCTION

The knowledge of thermal behavior is important to control the structure and properties of materials. For instance, processes as solidification at different rates can promote changes in materials properties. Several techniques have been utilized to investigate the kinetics of crystallization processes. The literature [1 – 4] demonstrates that thermoanalytical techniques (TA), such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are the most often applied. Several models [5 – 10] have been developed to reproduce experimental data under isothermal or continuous heating

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rate conditions. Quite surprisingly, the number of publications devoted to the kinetic analysis of solidification from the melt is relatively low. This situation may be attributed to the lack of theoretical models describing the solidification kinetics under continuous cooling conditions.

In this study, several methods are presented to analyze TA experimental data obtained under continuous cooling conditions. The methods were applied to the study of the solidification process of different polymer materials. The experimental and theoretical results are summarized in a temperature-cooling rate-transformation (T-CR-T) diagram.

2. KINETIC STUDY

In the modeling of the crystallization process, it's important to distinguish cold crystallization as against solidification from the melt. The main difference is that cold crystallization of a polymeric mixture may be promoted by pre-existing nuclei.

However, solidification from the assumed isotropic melt is expected to be driven by nucleation.

In the solidification process, a certain amount of undercooling, ($\Delta T = T_m - T$), where T_m is the melting temperature is necessary to induce solidification [11]. The driving force for nucleation is the Gibbs energy difference, ΔG, between the liquid and the crystal, which at low undercooling is proportional to ΔT: $\Delta G \approx \Delta S_f\ \Delta T$, with ΔS_f the melting entropy [12]. However, an interfacial energy, σ, is necessary to form the interface between the liquid and the nucleus. As a consequence, to be able to grow the size of the fluctuating forming nucleus has to be larger than a critical size. Irrespective of the mode of growth [13], nucleation is activated by a crystallization rate constant, k, which is proportional to some power of the nucleation frequency. The activation energy for homogeneous nucleation is of the form [14]

$$E = \frac{16\pi\sigma^3}{(\Delta G)^2} \tag{1}$$

Therefore, at low undercooling, one expects a rate constant of the approximate form

$$k(T) = A\exp(-B/T\Delta T^2) \tag{2}$$

where A has a smooth dependence on temperature with respect to the exponential factor and B is a constant proportional to $\sigma^3/\Delta S_m{}^2$.

Assuming the additive assumption [15] to derive kinetic data from thermoanalytical curve, the derivative of the degree of crystallinity, α, under a continuous cooling treatment at a constant rate, β, is

$$\frac{d\alpha}{dt} = \frac{kf(\alpha)}{\beta} \tag{3}$$

Under continuous cooling, the integrated form of this equation becomes [13]

$$g(\alpha) = \int_0^{\Delta T_o} \exp\left[\frac{-B}{T(\Delta T)^2}\right] \frac{d(\Delta T)}{\beta} \tag{4}$$

where the quantity g(α) is independent of the mode of crystallization (cooling or isothermal conditions). Several models allow us to obtain the T-CR-T curves from the knowledge of the values of the melting temperature and of the constant B. The approximate value of B can be obtained from the best fit approach to the experimental data under a constant cooling rate. The expression can be obtained from the frequency of nucleation on classical spherical model of heterogeneous nucleation [16], or by a procedure similar to the Kissinger method [13, 17]. The approximate value of B is

$$\frac{d \ln[\beta(3T_p - T_m)/T_p^2(T_m - T_p)^3]}{d(1/[T_p(T_m - T_p)^2])} \approx -B \tag{5}$$

where T_p is the peak temperature of the solidification process.

Another option, is to use a modified isoconversional method. The isoconversional method [18–20] was applied to find the activation energy on heating processes for a given degree of conversion. Here, it is adapted to evaluate the constant B in the case of solidification from the isotropic melt.

A basic assumption in the DSC technique is that the heat flow, Φ, is proportional to the conversion rate. Taking into account Eqs. (2) and (3), the following kinetic equation is obtained:

$$\Phi = \Delta H k(T) f(\alpha) = \Delta H A e^{-(B/T\Delta T^2)} f(\alpha) \tag{6}$$

Calculation of the constant B is based on a multiple-scan method that requires several measurements at different cooling rates. Taking logarithms from Eq. (6) yields

$$\ln\frac{\Phi}{\Delta H} = \ln[Af(\alpha)] - \frac{B}{T\Delta T^2} \tag{7}$$

The slope of $\ln(\Phi/\Delta H)$ *versus* $(1/T\Delta T^2)$ provides the constant B for a given α. If we repeat the procedure for different values of α, the invariance of B with respect to α (which is a basic assumption for the validity of the model) is checked in a simple and reliable manner. This operation allows testing the T_m accuracy at the same time. A first estimation of T_m results from previous heating, where samples are completely melted.

3. EXPERIMENTAL

The solidification process was analyzed here by means of differential scanning calorimetry (DSC). Experiments were carried out in a Mettler DSC30 equipment. The constant cooling rate measurements were performed at rates ranging from 2,5 to 60 K/min from the melt. In order to test the method, different polymeric materials were analyzed:

(A) Polypropylene–polyethylene (PP–PE), (PP rich 94% in weight) copolymer manufactured by Repsol and marketed as PPR 1042 with different commercial additives added to the base material.
(B) The PPR 1042 resin after 2000 hours of artificial aging.
(C) Mixture of a polyethylene glycol (85 wt%) with mean molecular weight between 5400 and 6000 (PEG 6000) and the drug SR 33557 developed by Sanofi Recherche.
(D) Mixture of PEG 6000 (70 wt%) with SR 33557.

Literature [21, 22], and previous results [23–25] lead us to state that solidification process depends on the molecular weight as well as on the thermal treatment of the polymer. It is known that the thermal history can affect the crystallization behavior of polymers. Furthermore, in the melting process the entanglement density should increase with time. It has been found that the degree of entanglement in the melt-state affects the crystallization [26]. Because of this, all samples of each material (A-B-C-D) were subjected to the same melt conditions.

Thanks to the differential scanning calorimetry technique applied to the study, we have obtained data on the temperatures and enthalpies of the whole process. Similar melting and cooling enthalpy was

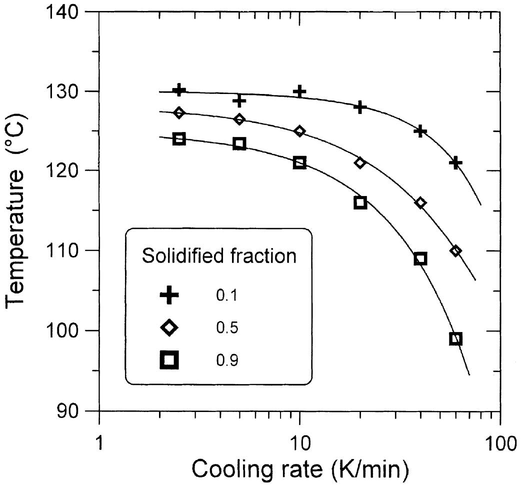

FIGURE 1 PP–PE as manufactured: calculated T-CR-T curves (solid lines) for the model and experimental DSC data (symbols).

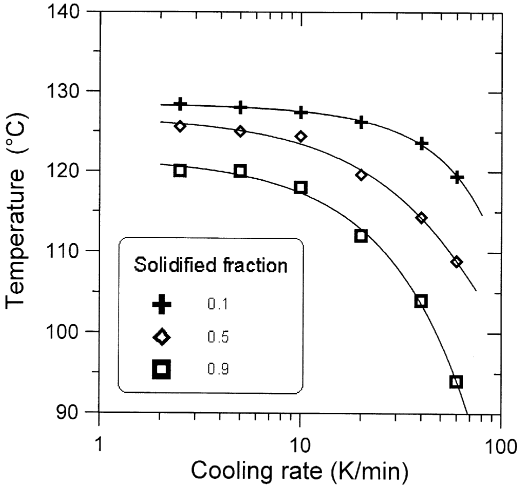

FIGURE 2 PP–PE (2000 hours of artificial aging): calculated T-CR-T curves (solid lines) for the model and experimental DSC data (symbols).

measured in all samples of each polymeric material, and samples were crystalline at all cooling rates. Moreover, similar mass (~8 mg) was used in all DSC experiments. From these data and with an adequate

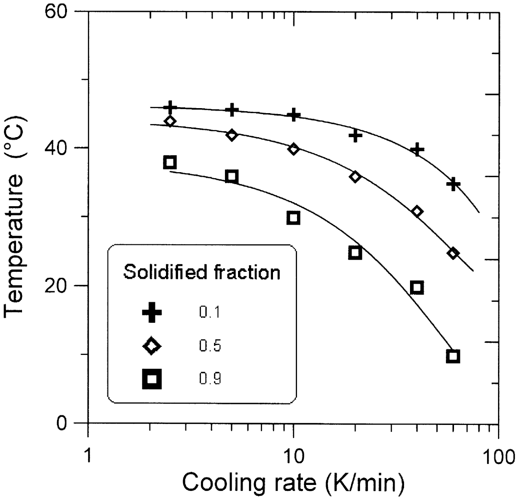

FIGURE 3 PEG 6000 (85 wt%)-SR mixture: calculated T-CR-T curves (solid lines) for the model and experimental DSC data (symbols).

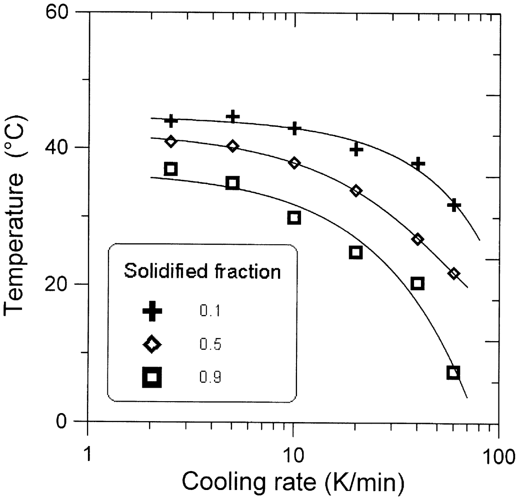

FIGURE 4 PEG 6000 (70 wt%)-SR mixture: calculated T-CR-T curves (solid lines) for the model and experimental DSC data (symbols).

theoretical model, understanding the behavior of polymers when treated thermally is possible.

Once B and T_m are known, temperature-cooling rate-transformation diagrams can be obtained from the kinetic model. Figures 1 to 4 show calculated (T-CR-T) curves (full lines) and several experimental DSC data for $\alpha = 0.1$, 0.5, 0.9. As expected in any solidification process, the solidification onset shifts to higher temperatures when the cooling rates decreases. We can state that the models give a good description of the solidification process.

4. CONCLUSIONS

The validity of a model to reproduce experimental data under dynamic conditions on cooling is tested. The driving force for nucleation is proportional to the undercooling. Moreover, a modified isoconversional method is applied to perform the thermal analysis of cooling processes. The solidification process of different polymer materials: polypropylene – polyethylene and mixtures of polyethylene glycol with drug was analyzed by means of differential scanning calorimetry. As expected, the onset of crystallization shifts to higher temperatures on decreasing the cooling rate.

Temperature-cooling rate-transformation diagram was constructed for a wide range of conditions and they showed a good agreement between experimental data and T-CR-T curves obtained by calculation. This verifies the reliability of the method utilized and the validity of the modified isoconversional model description.

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