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Improved experimental characterization of crystallization kinetics

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Abstract

Polymer solidification occurring in many processes, like for instance injection molding, compression molding and extrusion, is a complex phenomenon, strongly influenced by the thermo-mechanical history experienced by the material during processing. From this point of view, characterization of polymer crystallization in the range of processing conditions, i.e. including high cooling rate, is of great technological and academic interest. Quiescent, non-isothermal crystallization kinetics of two polypropylene resins were investigated using a new method, based on fast cooling of thin samples with air/water sprays and optical detection of the crystallization phenomenon. The range of cooling rates attained in this experimental study is considerably larger than that achieved by traditional methods. Quiescent crystallization kinetics of the resins is also investigated by the means of DSC, operated under isothermal conditions with a limited degree of under-cooling and for constant cooling rates up to about 1 K s^{-1}. The results demonstrate the importance of performing fast cooling experiments to gather reliable crystallization kinetics data.
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Keywords: Crystallization kinetics; Isotactic polypropylene; Real-time measurements

1. Introduction

It is well known that the final crystalline fraction in a polymer relates to the final products properties. This fraction is determined by the crystallization kinetics and the thermal and mechanical history of the material. In this paper, we will limit ourselves to the influence of the thermal history, specifically the cooling rate. Traditional methods for investigating the crystallization kinetics are usually limited to isothermal and/or slow heating/cooling rate analysis, mainly carried out using DSC technique. However, solidification during industrial processes occurs under much higher cooling rates than the ones involved in these experiments. The aim of this work is to present a recently developed method for characterizing crystallization kinetics at high cooling rates and to compare the performance of a well stated crystallization kinetics model, tuned by isothermal runs, to the experimental results, and, from that, to stress the need for such experiments.

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2. Materials and methods

2.1. Materials

The materials used were two different commercial iPP resins. The first one (a nucleated grade K2Xmod, Borealis, $M_w = 365{,}000$, $M_n = 67{,}000$), was studied before by traditional methods also by Zuidema et al. [1], who found a temperature only dependent density of nuclei and growth rate

$$N(T) = n_1 T + n_2 \qquad (403 \div 413\ \text{K}), \tag{1}$$

$$G(T) = G_{\max} \exp\left[-2\frac{(T - T_{\text{ref}})^2}{\beta}\right] \qquad (363 \div 393\ \text{K}), \tag{2}$$

where $n_1 = -2.6087 \times 10^{13}\ \text{m}^{-3}\ \text{K}^{-1}$, $n_2 = 6.5783 \times 10^{15}\ \text{m}^{-3}$, $G_{\max} = 8.1 \times 10^{-6}\ \text{m s}^{-1}$, $T_{\text{ref}} = 356.8\ \text{K}$, $\beta = 1126.9\ \text{K}^2$.

The second one (non-nucleated grade T30G, Montell, $M_w = 481{,}000$, $M_n = 75{,}000$) was also studied previously, by Lamberti [2]. The isothermal half-crystallization time, i.e. the time at which 50% of final crystallinity content is obtained, was determined with a standard DSC apparatus (Mettler DSC30) and described by

$$\frac{1}{t_{1/2}(T)} = \frac{1}{t_{1/2}^0} \exp\left[-\frac{U}{R \cdot (T - T_g^0 + T_\infty)}\right]$$
$$\cdot \exp\left[-\frac{\kappa_2 \cdot (T_m^0)^2 \cdot (T_m^0 + T)}{2T^2 \cdot (T_m^0 - T)}\right], \tag{3}$$

where $t_{1/2}^0 = 5.75 \times 10^{-15}\ \text{s}$, $U/R = 2068.8\ \text{K}$, $\kappa_2 = 3.171$, $T_g^0 = 263.15\ \text{K}$, $T_m^0 = 463.15\ \text{K}$ and $T_\infty = 51.6\ \text{K}$.

Eder and Janeschitz-Kriegl [3] studied the growth rate of iPP alpha phase, for several iPPs. Data analysis was performed on the basis of the Lauritzen and Hoffmann equation (Eq. (38) on page 559 in [4]) in which the coefficients K_g has been substituted by $\kappa_3 T_{m0}^2$ and the correction factor f ($f = 2T/(T_m^0 - T)$, as given by Eq. (10b) on page 540 in [4]) has been directly inserted in the second exponential term

$$G(T) = G_0 \exp\left[-\frac{U}{R \cdot (T - T_g^0 + T_\infty)}\right]$$
$$\cdot \exp\left[-\frac{\kappa_3 \cdot (T_m^0)^2 \cdot (T_m^0 + T)}{2T^2 \cdot (T_m^0 - T)}\right] \tag{4}$$

with $G_0 = 4.36 \times 10^8\ \text{m s}^{-1}$ and $\kappa_3 = 2.7979$. Assuming a dependence on temperature only of the nuclei density as well as of the growth rate, it is straightforward to obtain [2,5]

$$N(T) = \frac{\ln(2)}{\frac{4\pi}{3} G(T)^3 t_{1/2}(T)^3} \tag{5}$$

leading to the expression for the nuclei density that is used in this work. Eqs. (3)–(5) are used to describe the crystallization kinetics of the grade T30G. The model proposed does not take in account for regime transition at different under-cooling, i.e. the parameter κ_3, which should change with crystallization regime, has been taken as a constant.

2.2. Methods

Slow cooling runs in addition to isothermal tests were performed using differential scanning calorimetry (Mettler DSC30). The crystallinity evolution during DSC tests was evaluated by applying a correction to the data as was suggested by Eder and Janeschitz-Kriegl [3]. The equivalent heat transfer coefficient γ was evaluated from temperature relaxation after melting indium. A value of $14.5\ \text{mW K}^{-1}$ was found.

Fast cooling runs were carried out by means of a new method described in detail elsewhere [6]. A schematic of the apparatus is depicted in Fig. 1. It includes a hot (oven) section and a cold (quench) section. Sample heating is attained by two radiating electric heaters while the cooling is done with a couple of nozzles that spray both faces of sample holder with gas or gas–liquid (typically air and water). This cooling system was designed to cover a large range of cooling rates (from 0.01 to 500 K s^{-1}). As shown in Fig. 1, the polymer sample, a thin film with an embedded thermocouple is confined between two thin glass slides that acts as a sample holder. In turn, the glass slides are fastened to a sliding rod, which can be quickly shifted from the hot to the cold section. In a typical experiment the transmitted light and temperature are monitored during the spraying of the sample holder [6].

Experimental tests confirmed a satisfactory reproducibility of the tests in the same conditions, i.e. at the same cooling rate.

The evolution of the crystallinity during quench experiments was determined by applying a recently proposed analysis of the transmitted overall light $I_O(t, S)$ [6], in which S is the thickness and t is the time. According to this analysis, the degree of space filling ξ_g is given by

$$\xi_g(t) = \frac{1}{2S\sigma_0}\left\{ S\sigma_0 + \ln\left(\frac{I_{O,i}}{I_{O,f}}\right) - \sqrt{\left[\ln\left(\frac{I_{O,f}}{I_{O,i}}\right)\right]^2 + S\sigma_0[S\sigma_0 - 2(\ln I_{O,i} + \ln I_{O,f}) + 4\ln I_O(t, S)]} \right\}, \tag{6}$$