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 undercooling 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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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

$$N(T) = n_1 T + n_2 \quad (403 \pm 413 \text{ K}),$$

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

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

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). 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 $\gamma$ was evaluated from temperature relaxation after melting indium. A value of 14.5 mW K$^{-1}$ was found.

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 $\gamma$ was evaluated from temperature relaxation after melting indium. A value of 14.5 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 $I_0(t, S)$ [6], in which $S$ is the thickness and $t$ is the time. According to this analysis, the degree of space filling $\xi_g$ is given by

$$\xi_g(t) = \frac{1}{2S\sigma_0} \left\{ S\sigma_0 + \ln \left( \frac{I_{0,t}}{I_{0,i}} \right) - \sqrt{\left[ \ln \left( \frac{I_{0,t}}{I_{0,i}} \right) \right]^2 + S\sigma_0 [S\sigma_0 - 2(\ln I_{0,i} + \ln I_{0,t}) + 4 \ln I_0(t, S)]} \right\}.$$
\[ \sigma_0 = \ln \left( \frac{I_{0,i}}{I_{0,f}} \right) \frac{1}{S(2\xi_{g,\text{peak}} - 1)}. \]  

(7)

The value \( \xi_{g,\text{peak}} \) is the degree of space filling at which a maximum in the light intensity is found. It can be evaluated \[6\] by

\[ \xi_{g,\text{peak}} = \left[ \ln \left( \frac{I_{0,i}}{I_{0,j}} \right) \right]^{-1} \left[ \ln \left( \frac{I_{0,\text{min}}}{I_{0,j}} \right) \right] + \sqrt{\ln \left( \frac{I_{0,i}}{I_{0,\text{min}}} \right) \ln \left( \frac{I_{0,j}}{I_{0,\text{min}}} \right)}. \]  

(8)

where \( I_{0,\text{min}} \) is the minimum recorded light intensity.

The half-crystallization temperature was determined as the temperature at which the crystallinity level was equal to one half of the final level (long time) attained at the end of cooling runs both for DSC and quench tests.

3. Modeling

Crystallization kinetics was modeled following the same approach as used by Zuidema et al. \[1\] using Schneider et al. rate equations \[7\], i.e. by solving the following set of nested differential equations:

\[
\begin{align*}
\dot{\phi}_1 &= 8\pi \tau, \\
\dot{\phi}_2 &= G\phi_3, \\
\dot{\phi}_3 &= G\phi_2, \\
\dot{\phi}_0 &= G\phi_1.
\end{align*}
\]

(9)

where \( \phi \) is the time derivative of nuclei density, and \( \phi_i \) are auxiliary variables used to describe morphology of undisturbed crystals. The Kolmogoroff–Avrami–Evans approach was applied to account for spherulites impingement

\[ -\ln(1 - \xi_g) = \phi_0, \]  

(10)

where \( \xi_g \) is the degree of space filling or relative crystallinity. The absolute degree of crystallinity \( \xi \) is simply obtained by multiplying the degree of volume filling \( \xi_g \) by a local constant degree of crystallinity \( V_\infty \) of spherulites (the so called “equilibrium crystallinity”). For high cooling rate tests, when the degree of space filling \( \xi_g \) does not level to unity, even for long times, the remaining fraction of material volume is assumed to be mesomorphic, leading to a material consisting of spherulites embedded in a mesomorphic matrix \[1\]. A fourth order Runge–Kutta method was used to solve numerically Eqs. (9) and (10).

4. Results and discussion

Fig. 2 shows the experimental determined degree of space filling from DSC tests after data correction according to Eder and Janeschitz-Kriegl \[3\]. Model predictions, using the parameter values given in Section 2.1, are also reported. The comparison shows that a reasonable qualitative but a poor quantitative agreement. The predictions overestimate the crystallization rate at 0.033 K s\(^{-1}\), are fairly in agreement at 0.17 K s\(^{-1}\) and underestimate the kinetics at 0.50 K s\(^{-1}\), pointing out a too low dependency of the model crystallization rate on temperature. Moreover,
the qualitative trend is not satisfactory at high crystallinity levels, i.e. at low temperatures, where the predictions level to unit value, attained from crystallization at low temperatures, i.e. for very long crystallization times. This experimental result is most probably due to secondary crystallization that is not taken into account in the crystallization kinetics model used here. The temperature gap between prediction and data is however restricted to few degrees, stating that the model fairly well predicts the crystallization behavior for low cooling rates (DSC experiments).

Fig. 3 reports the measured and predicted degree of space filling during quenching tests. It is worth noticing that characteristic cooling rates (defined at 343 K [8]) are much higher than the cooling rates attainable in DSC tests.

The comparison shows that the quantitative agreement is even worse than in case of DSC experiments, i.e. the low cooling rates. The predictions, strongly underestimate the crystallization rate for all experiments. Moreover, the gap between experimental data and model predictions increases for an increasing cooling rate, confirming the too weak dependence of model crystallization rate on temperature.

A better, simplified way to outline the difference between model predictions and the experimental data is
provided by Fig. 4 where experimental and predicted half-crystallization temperatures are reported versus characteristic cooling rates for both materials.

Based on past experience and the rather good agreement found here, the characteristic cooling rate as defined above was adopted as the parameter that consistently represents the thermal history of the sample for quench tests.

For both materials the model predicts fairly well the low cooling rate crystallization behavior, whereas it loses its reliability at higher cooling rates, where it strongly underestimates the crystallization temperature, the difference becoming larger with increasing cooling rate for both materials. Since the isothermally tuned model is not able to describe the high cooling rate tests, these experiments confirm the need for an extended description of the crystallization kinetics under high cooling rates.

5. Conclusions

For two materials, a nucleated and a non-nucleated iPP, the crystallization kinetics model parameters, determined from experiments under isothermal conditions:

(i) Provide a fairly satisfactorily description of slow cooling rate tests, performed with traditional DSC, suggesting that simple, standard experiments, can provide the parameter values that reliably describe crystallization kinetics.

(ii) Are not able to provide a satisfactory description of crystallization kinetics during high cooling rates. In particular, they strongly underestimated the half-crystallization temperature, leading to a severe limitation of their applicability in modeling/simulation of polymer transformation processes that typically involve high cooling rates.

The models used here, are insufficient to describe the real behavior of a crystallizing iPP (for example, Fig. 6 in [9]). It is required to account for another phase developing in the same temperature range [10] or to modify the kinetic model, for example with a cooling rate dependent term [9]. However, to work out this issue is beyond the scope of the present paper.

Summarizing: the model, proposed and tuned to describe the isothermal crystallization, was found to describe the isothermal as well as the slow cooling rates tests (confirming the validity of parameters value found by tuning), whereas the model was found largely inaccurate in description of high cooling rates tests. Thus, there is the need for improvement in modeling to describe the high cooling rates behavior, accounting for different phenomena.

The results reported in this work emphasize the need of using crystallization data gathered under “processing condition” for model tuning. Only in this way, a reliable description of the crystallization behavior can be obtained.

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