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Morphology Evolution During Polymer Crystallization Simultaneous Calorimetric and Optical Measurements

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Summary: The crystallization of the isotactic poly(propylene) (I-PP) has been studied carrying out measurements by means of a special calorimeter connected to a microscope and a digital acquisition system of images. To authors' knowledge, this is the first time that simultaneous calorimetric and optical measurements are carried out on polymers. The analysis of Polarized Optical Microscopy images has allowed the appraisal of nucleation density and growth rate in isothermal and non isothermal conditions. The results obtained in isothermal conditions have been analyzed through the Kolmogoroff model and the crystallinity calculated from the model has been compared with that obtained from the calorimetric measurements.

Keywords: calorimetry; crystallization; poly(propylene) (PP); spherulites

Introduction

Calorimetry and polarized optical microscopy are commonly adopted techniques in the study of polymer crystallization. Calorimetry allows the determination of the evolution of the crystalline degree through the latent heat of crystallization. Information about the evolution of morphology inside the sample cannot be obtained by this technique. On the other hand, optical microscopy allows the direct determination of the evolution of morphological characteristics of the sample, which in quiescent conditions essentially mean number of nuclei and spherulite dimensions (radii). Despite of the fact that both techniques provide data about the same phenomenon, it is still under discussion which is the appropriate relationship linking the resulting data. The aim of this work is the study of crystallization kinetics of isotactic poly(propylene) (I-PP), by coupling the two techniques in simultaneous measurements through a novel transparent single cell system from Linkam Scientific Instruments.[1] The present study constitutes a preliminary step using this new technique on a well known system. The Kolmogoroff-Avrami-Evans (KAE) model was adopted to relate the two sets of data.

Experimental

Material

The material used in this work was a commercial I-PP resin (non-nucleated grade T30G, Montell, $M_w = 376000$, $M_w/M_n = 6.7$, tacticity = 87.6%mmmm). Crystallization kinetics of this material was characterized in the literature by adopting the Kolmogoroff model.[2] In particular, the following expressions were used in order to describe the growth rate and the nucleation density as functions of temperature:

$$G[T(t)] = G_0 \exp\left[-\frac{U}{R(T(t)-T_\infty)}\right] \times \exp\left[-\frac{K_g(T(t)+T_m)}{2T^2(t)\cdot(T_m-T(t))}\right] \quad (1)$$

$$N[T(t)] = N_0 \exp[\beta(T_m - T(t))] \quad (2)$$

The kinetic parameters used in the Eqs. (1) and (2) are $N_0 = 17.4\cdot10^6$ nuclei/m^3,

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$\beta = 0.155\ \mathrm{K}^{-1}$, $K_g = 534858\ \mathrm{K}^2$, $G_0 = 2.1 \cdot 10^{10}\ \mu\mathrm{m/s}$, $T_\infty = 236\ \mathrm{K}$, $U/R = 755\ \mathrm{K}$, $T_m = 467\ \mathrm{K}$.[2]

These parameters were found by best fitting data of crystallization kinetics in a very wide range of conditions, both isothermal and non-isothermal at cooling rates as high as 500 K/s.

Eq. (2) assumes heterogeneous nucleation, i.e. a number of nuclei per unit volume which depends only on temperature.

Calorimetric and Optical Measurements

A special calorimeter (Linkam DSC600, calibrated with Indium, cooled with liquid nitrogen and purged with nitrogen) was adopted for the experiments. The cell has thin glass windows (thickness and diameter, 160 μm and 7 mm respectively) on both sides and the sensing element is pierced (diameter 1.5 mm) in order to allow the direct observation of the sample.

The crystallization kinetics was investigated in isothermal and non isothermal conditions. In isothermal tests the material was tested at the following temperatures: 121 °C, 123 °C, 125 °C. In non isothermal tests, two cooling rates were imposed: −5 K/min, −20 K/min.

The sample (a thin film, thickness about 100 μm, weight about 1 mg) was heated from 25 to 240 °C, and kept at 240 °C for 30 minutes to erase the previous thermomechanical history. In isothermal tests, the sample was then quickly cooled (−120 K/min) to the test temperature, at which it was kept until complete crystallization. In non isothermal tests, the sample was cooled from 240 °C to ambient temperature adopting a constant cooling rate. During all calorimetric tests, the heat released during the crystallization was measured. The fraction of material crystallized after a time t, was calculated from the equation:

$$\xi(t) = \frac{\int_{t=0}^{t} dH(t)}{\int_{t=0}^{\infty} dH(t)} = \frac{\Delta H_t}{\Delta H_{TOT}} \tag{3}$$

where $\xi(t)$ is the degree of space filling, and the first integral is the heat generated at the time t and the second is the total heat, when the crystallization is complete.

The morphology and the isothermal growth of the spherulites was observed using a confocal microscope (Olympus BX41) coupled to the Linkam DSC600, during the calorimetric tests.

The micrographs, acquired at suitable time intervals with crossed polarizer, in isothermal conditions (T = 123 °C) show, as reported in Figure 1, the growth of crystalline structures. During all the isothermal tests carried out, it could be observed that all nuclei were generated simultaneously and their number did not change with time. This is a confirmation that at each temperature the nucleation density is constant, consistently with the hypothesis of Eq. (2). It is important to notice that, when the spherulites diameter is small if compared with film thickness (100 μm), spherulites growing on different planes are present in the pictures.

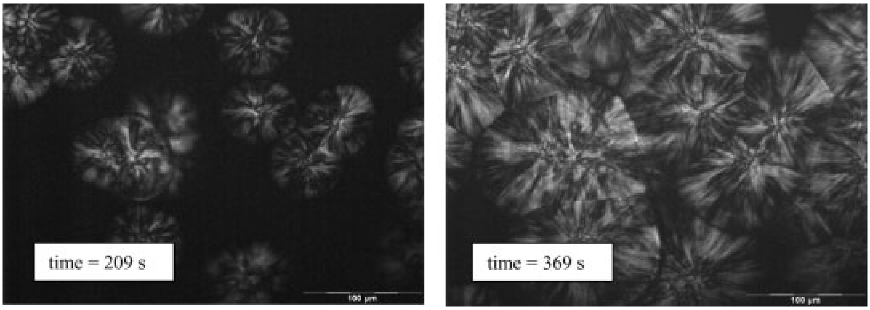

Figure 1.
Micrographs during isothermal crystallization (magnification 20x, crossed polarizers), test temperature = 123 °C.

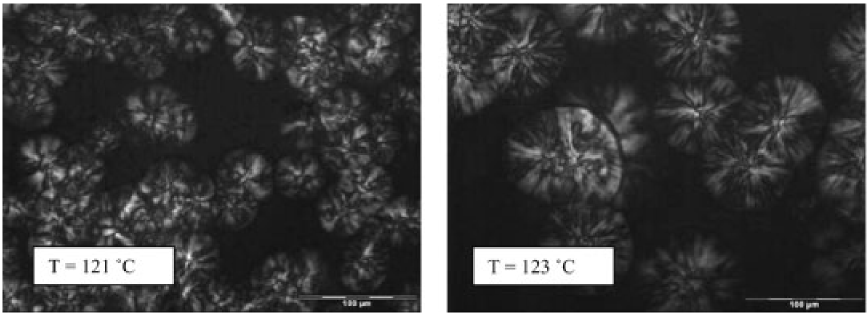

Figure 2.
Micrographs during isothermal crystallization (magnification 20x, crossed polarizers), at the same crystallinity degree of 20% evaluated by calorimetric measurement, from Eq. 3.

During all performed tests, β spherulites were not observed, in agreement to previous studies performed on the same material.[2] The simultaneous calorimetric and optical measurements allowed to relate directly the observed structure to an overall crystallinity degree, avoiding any effect related to even small differences in thermal history or samples geometry and dimensions. A typical result of such measurements is reported in Figure 2, where a comparison between two pictures taken during isothermal tests at two different temperatures (namely 121 °C and 123 °C) is shown. Both pictures refer to the same relative crystallinity degree, evaluated from calorimetric measurements, by the means of Eq. 3, as about 20%. As clear from the micrographs, the lower is the temperature, the higher is the number of the spherulites and the smaller is their radius, so that the remaining amorphous volume (resulting as black even during a sample rotation between crossed polarizers in Figure 2) is the same.

Nucleation Measurements

Nucleation density was measured for each test by counting the number of spherulites, N, present on the observed surface (A), at the end of crystallization.[3] The volumetric density N_v was calculated as [4]

$$N_V = \left(\sqrt{\frac{N_A}{1.458}}\right)^3 \tag{4}$$

where N_A is the surface density of nuclei.

A comparison between experimental data retrieved during the isothermal tests and model predictions (from Eq. 2) is reported in Figure 3. The agreement is satisfactory, although not perfect. This difference could be due to the excessive magnification that induces the observation of a number of nuclei (of the order of 10) statistically not enough meaningful. It should be pointed out, however, that such a magnification is a compromise between the measurements of nucleation density (which would suggest to analyze a large surface) and of growth rate (which requires accurate determination of spherulite diameter and thus a large magnification).

Measurements of nucleation density was also performed during non isothermal tests.

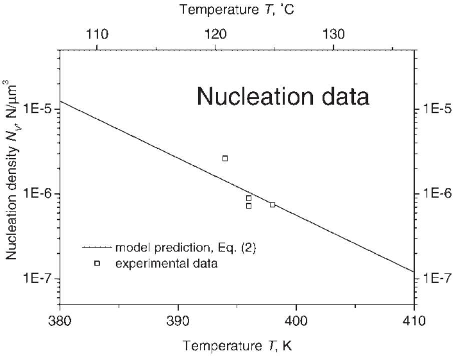

Figure 3.
Experimental data of nucleation density in isothermal conditions and model prediction from Eq. (2).

For this kind of tests, volumetric density N_v was evaluated directly by dividing the number of observed nuclei by the field of vision times the thickness of the film. These measurements allow to obtain, from just one cooling test, a whole curve of number of nuclei present inside the sample at each temperature. Of course the procedure is complicated by the fact that the number of nuclei changes with the temperature, and thus increases on increasing time. The main limit of such measurements concerns the fact that a nucleus is recognized as such when it reaches a radius, R_{vis}, which depends on the adopted magnification. This means that the temperature at which the nucleus is counted, $T_{apparent}$, is somewhat lower than the temperature at which it was generated, T_{true}. The two temperatures are linked by the following relationship

$$\int_{T_{true}}^{T_{apparent}} \frac{G(T)}{\dot{T}} dT = R_{vis} \qquad (5)$$

where G(T) is the growth rate. During the tests conducted in this work, R_{vis} was 5 μm.

Data of nucleation density obtained in non isothermal conditions are shown as symbols in Figure 4. Two series of data are shown, each of them reporting the number of nuclei measured during the cooling test, but reported versus a) the raw, uncorrected temperature at which the measurement was performed (open symbols); b) a corrected T_{true} temperature, calculated by means of Eq. (5), considering $R_{vis} = 5$ μm, consistently with the adopted magnification (full symbols). As a reference, also model predictions (from Eq. 2) are reported in Figure 4 (full line). Again, the collected data lay around the line representing model predictions, and the deviations are within a factor 2. Obviously, the lowest is the applied cooling rate, the more accurate are the measurements, since the phenomenon is slower. However, higher cooling rates allow to investigate a wider temperature range.

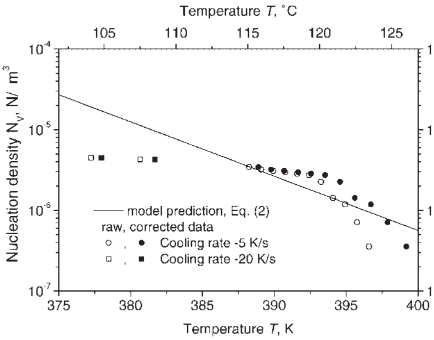

Figure 4.

Experimental data (raw data as open symbols, corrected data, through Eq. 5 with $R_{vis} = 5$ μm, full symbols) of nucleation density in non isothermal conditions (dT/dt = −5 K/min, dT/dt = −20 K/min), and model prediction, from Eq. (2).

Growth Measurements

The growth of the spherulites was followed by analyzing the variation of the radius of each spherulite in the micrographs at appropriate time intervals until impingement.

Figure 5 reports the time evolution of spherulite radii during the isothermal tests. The data confirm that at each temperature the growth rate of the spherulites, G(T) (namely the slope of each plot) is constant.

The radial growth rates calculated by analyzing the data reported in Figure 5 are compared with model prediction, using Eq. (1), in Figure 6. The agreement between data and prediction is considerable, confirming the reliability of the growth measurements.

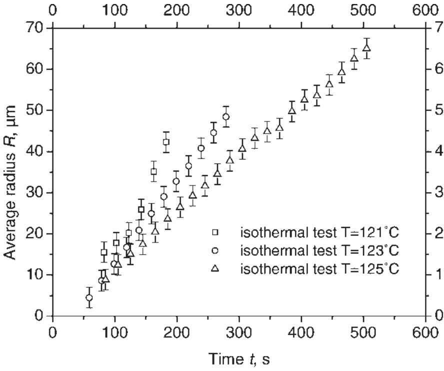

Figure 5.

Time evolution of spherulite radii during isothermal tests.

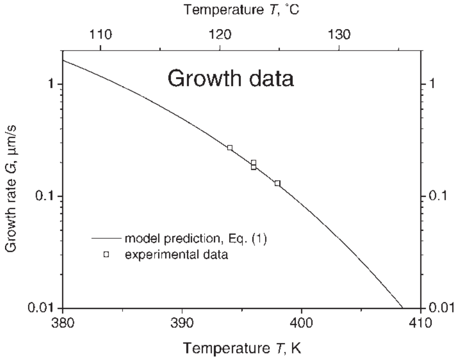

Figure 6.
Experimental data of nucleation growth rate in isothermal conditions, and model prediction from Eq. (1).

Also non-isothermal tests allow the determination of growth rate. Again, the method is complicated by the fact that the growth rate is not constant during the test. The procedure followed in this work can be schematized as

- measurement of radial evolution with temperature by analyzing the micrographs
- best fitting of the result by means of a polynomial function
- analytical derivation of the obtained function

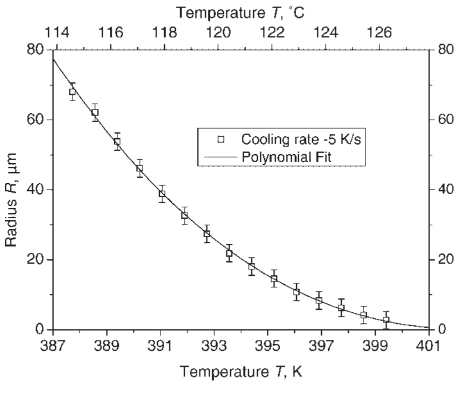

Figure 7.
Time evolution of spherulite radius and polynomial data fit during a non isothermal test, cooling rate −5 K/s.

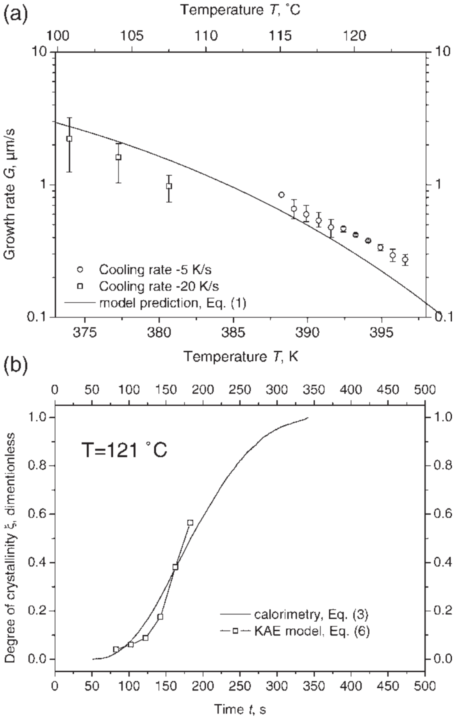

Figure 8.
(a) Experimental data of nucleation growth rate in non isothermal conditions (dT/dt = −5 K/min, −20 K/min), and model prediction from Eq. (1). (b) Evolution of relative degree of crystallinity for the isothermal test at 121 °C.

About ten spherulites were followed during each cooling test. The time evolution of one of them during a cooling ramp at −5 K/min is reported in Figure 7.

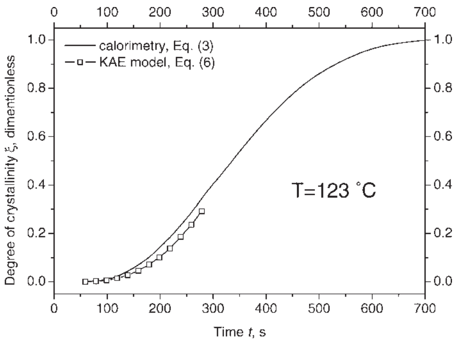

Figure 9.
Evolution of relative degree of crystallinity for the isothermal test at 123 °C.

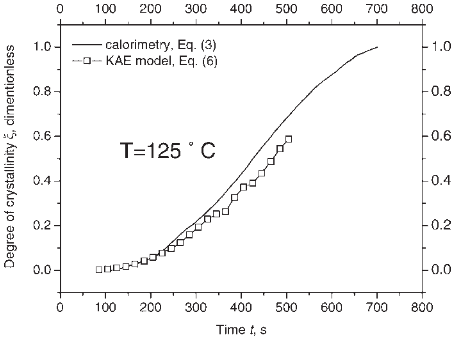

Figure 10.
Evolution of relative degree of crystallinity for the isothermal test at 125 °C.

Experimental data of radial growth obtained in non isothermal conditions are shown in Figure 8, together with the model prediction (Eq. 1).

Discussion

The KAE model directly relates the morphological characteristics, namely nucleation density and spherulite radii, to the evolution of the degree of space filling, through the following equation:

$$\xi(t) = 1 - \exp\left(-\frac{4}{3}\pi N_V R^3\right) \qquad (6)$$

The degree of space filling, estimated through Eq. 6, was compared, in Figures 8, 9 and 10, with calorimetric measurements, which provide crystallinity evolution through Eq. (3).

In all the tests carried out a substantial agreement of the calorimetric data with the Kolmogoroff model predictions, through the experimental measurements of nucleation and growth, was found.

Conclusion

In this work simultaneous measurements of calorimetry, nucleation and growth of crystalline structures have been carried out using an novel transparent calorimeter. The measurements of nucleation and growth, obtained during both isothermal and non-isothermal tests, have been compared with a model present in the literature, showing a good agreement, in particular for the growth rate. In isothermal conditions, the evolution of the crystalline degree, estimated replacing experimental data of nucleation and growth in the kinetic equation of Kolmogoroff, has been compared successfully with the crystallization measured from the calorimeter.

The technique adopted in this work has shown to be a powerful mean of investigation. Further applications of the technique to other systems are currently in progress.

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