Delay in the growth of polymer spherulites caused by superheating

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Kinetics of crystal growth has considerable importance in industry, either for the influence on production time or on the mechanical properties of the resulting goods [1]. Heat transfer from a crystallizing substance to the surroundings is indispensable for the crystallization to proceed [2]. Otherwise, the temperature of the substance would increase and, according to the thermodynamics, the solid–liquid equilibrium be shifted in favour of the liquid phase. The local arrest of crystallization because of superheating at the growth front is a well-known phenomenon for metals, readily identified since it leads to characteristic dendritic morphologies [3]. The recognition of superheating at the growth front of polymer spherulites is not as obvious as for metals. Indeed, because of the slow crystallization rate of polymers relative to metals, such a phenomenon would go unnoticed under conventional isothermal crystallization since neither a variation of the circular shape of spherulites nor an appreciable deceleration of the radial growth rate can be usually produced. However, the mathematical relationship between the radius of polymer spherulites and the radial growth rate calculated under isothermal conditions may be exploited to derive the theoretical change of the dimension of a spherulite growing under nonisothermal conditions in the absence of superheating. Comparing this value to the experimental datum, it is possible to draw information on the occurrence of superheating phenomena.

In this work a method is shown to demonstrate the deceleration of polymer spherulites as a consequence of superheating. The method consists in measuring the increase of the radius of spherulites while the external temperature is increased in the range where crystallization occurs. Despite the invariability of the exterior spherulitic structure on the optical scale, the deceleration of the crystal growth during heating may be proved on the basis of the comparison between the theoretically predictable enhancement of spherulite size and the experimental value. Isotactic polypropylene with a small amount (2.4 wt%) of ethylenic units randomly distributed along the chain has been used in the present investigation. The product (E/P), having weight-average molecular weight $M_w = 216\,000$, was kindly supplied by Montell Polyolefins Company (Ferrara, Italy) and used, instead of isotactic polypropylene homopolymer, because of its wider crystallization temperature range [4].

The following experimental procedures were adopted. For optical observations during crystallization, a small amount of E/P was squashed between two glass slides to give tens of micrometers thick film. Specimens were then inserted in a Linkam THMS 600 hot stage programmed by a TMS91 unit.

In isothermal crystallization, specimens were kept at 473 K for 600 s in order to destroy any previous trace of crystallinity and then the temperature rapidly decreased (with a scan rate of -0.5 K/s) to the selected crystallization temperature in the range 393–413 K. The hot stage device was maintained at a constant temperature until primary crystallization was completed. In nonisothermal procedures, the temperature was kept at 473 K for 600 s, and then rapidly decreased to 393 K, allowing nucleation to that temperature, and finally increased at 0.0833 K/s during crystallization up to 413 K. A Zeiss polarizing microscope equipped with a JVS TK-1085E video camera was used for images acquisition. Pictures were taken at appropriate instants of time and the radius of spherulites measured with Image-Pro Plus software in order to estimate the linear growth rate. A graduate grid was used for length calibration.

The radial growth rate G of spherulites is achievable by measuring the radius r of spherulites as a function of time t. The slopes of the isothermal lines resulting in r–t plots provided the values of G as function of temperature. Values of G in the explored temperature range are reported in Table I; the equation between G and T may be obtained by means of the least square method. This procedure, applied to E/P crystallization in the range 393–413 K, resulted in the following equation:

$$G = 1.701 \times 10^{31} \mathrm{e}^{-0.2222T} \tag{1}$$

Further processing of Equation 1 allows the calculation of the increase of the radius of spherulites, originated at a certain temperature T_i, by heating from T_i to a higher temperature T_f. Considering the temperature varying linearly with time and designating the heating rate with v, that is,

$$T = vt + T_i \tag{2}$$

the function $G(T)$ can be expressed as function of the heating time $t = (T - T_i)/v$ by associating at each time t the value of G corresponding to the temperature T. The reference time $t = 0$ corresponds to the instant of time at which $T = T_i$ before the heating start.

For instance, during heating at 0.0833 K/s from 393 to 413 K, the radial growth rate expressed by (1) varies as a function of time according to the equation:

$$G = 2.017 \times 10^{-7} \mathrm{e}^{-0.01852t} \tag{3}$$

According to the theory of error propagation, the absolute value of the error δG on the growth rate data may be obtained as follows:

$$|\delta G| = \left|\frac{dG}{dt}\right| \cdot |\delta t| = 2.017 \times 10^{-7}$$

$$\times 0.01852 \times e^{-0.01852t} \times |\delta t| \qquad (4)$$

For each time t the error $|\delta G|$, calculated by (4) assuming that error on time $|\delta t|$ is 0.252 s (corresponding to the acquisition time of the camera), is reported in Table I.

As G is the derivative of r with respect to t, r is a primitive function of G, that is,

$$\Delta r = r_f - r_i = \int_{t_i}^{t_f} G(t)\,dt \qquad (5)$$

Thereby the increase of the radius during the 240 s of heating in the range 393–413 K may be obtained by definite integration of $G(t)$:

$$\Delta r = \int_0^{240} 2.017 \cdot 10^{-7} e^{-0.01852}dt$$

$$= (-2.017 \cdot 10^{-7}/0.01852)(e^{-4.4448} - e^0)$$

$$= (1.08 \pm 0.02) \cdot 10^{-5}\,\text{m} \qquad (6)$$

The value derived from (6) would be that expected if the growth under nonisothermal conditions entailed instant by instant heat dissipation rates identical to those governing isothermal crystallization. In other words, (5) is applicable in absence of superheating phenomena. However it was found that heating during crystallization hinders heat exchange with the surroundings, causing superheating with a consequent reduction of the crystallization rate $\Delta r/\Delta t$ predicted on the basis of isothermal G data. Indeed, poor heat dissipation causes heat accumulation at the growth front, consequently reducing the crystal growth rate relatively to isothermal procedures.

For instance, the experimental increase of r during heating of E/P spherulites at 0.0833 K/s from 393 up to 413 K is about 7×10^{-6} m, a value far lower than that predict, namely 1.08×10^{-5} m. It is worthy of note that the sum of the errors on the radius, calculated by the formula $|\delta r| = G \cdot |\delta t| = 2.017 \times 10^{-7} \times e^{-0.01852t} \times |\delta t|$ and also reported in Table I, is 1.41×10^{-7} m. Hence 2×10^{-7} m represents the maximum error on the expected value of Δr. The small error on Δr demonstrated that the difference between the theoretical and experimental values of Δr is not justifiable by the error entailed by the mathematical processing of data. Therefore this difference must be ascribed to the occurrence of heat accumulation which slows down the crystallization of the polymer in the range 393–413 K, reducing the growth rate from an average theoretical value of 4.5×10^{-8} m/s to 2.9×10^{-8} m/s. This deceleration proves the existence of superheating phenomena in the polymer under crystallization conditions that prevent a rapid heat exchange. Moreover, this phenomenon could be associated to the branching in spherulites of the stable α phase of polypropylene [5–7], as accumulation of heat at the growth front of parent lamellae could favour the development of daughter lamellae in cooler directions on the solid–melt interface.

In conclusion, by comparing the prediction of the growth of spherulites on a theoretical basis to the experimental increase of dimensions, the importance of heat removal during an exothermal process, such as crystallization, has been demonstrated for E/P.

References

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