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A direct way to determine iPP density nucleation from DSC isothermal measurements

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Summary

In the present work, a large number of growth rate data for α-phase isotactic polypropylene, taken from literature, have been described by the Lauritzen and Hoffmann equation. A general procedure to predict nuclei density by simple DSC measurements is described and applied successfully to a commercial iPP.

1. Introduction

The crystallization of polymers involves a lot of phenomena of great importance in polymer science and in polymer processing. Despite of the huge amount of work done to analyze and to describe all these phenomena, models to implement in process simulation are not fully reliable yet.

Starting from early works of Kolmogoroff [1], Avrami [2] and Evans [3], the crystallization kinetics have been modeled in term of degree of space filling and impingement between growing entities. The growth phenomena has been described by Lauritzen and Hoffmann [4], while the nucleation theory has received fundamental impulse from the work of Ziabicki [5, 6]. An excellent review of the data and of the model available is the work of Eder and Janeschitz-Kriegl [7].

Kinetic models to be used in process simulation have to correctly take into account the effects of external conditions on crystallization kinetics: temperature, rate of cooling, pressure, flow, other external forces. The isothermal modeling, at room pressure and in quiescent conditions, is well established, the most difficult part of the work is to estimate the material functions.

Aim of this work is to point out a way to estimate isotactic polypropylene nuclei density from growth rate data and from semi-crystallization time measurements by DSC.

2. Summary of the model equations

The kinetics of *degree of space filling*, ξ_g, during polymer crystallization is usually described by the well-known Kolmogoroff-Avrami-Evans equation (KAE equation) [1-3]:

$$\xi_g(t) = 1 - \exp[-E(t)] \qquad \textbf{(1)}$$

where $E(t)$ is the *expectancy* of the crystalline phase, i.e. the volume that the crystals would occupy if no impingement occurs. The expectancy can be calculated with a model in which all the phenomena involved are lumped in a single material function, the overall rate of crystallization, k, or the semi-crystallization time, $t_{1/2}$, as follows:

$$E(t) = kt^m = \ln(2)\left(\frac{t}{t_{1/2}}\right)^m \qquad \textbf{(2)}$$

where m is the Avrami exponent, accounting for crystallite dimensionality and for nucleation kind (pre-determined or sporadic). The expectancy can be calculated also with a more sophisticated model, which uses more material functions, the nuclei density N or the nucleation rate α and the growth rate G [5-6]:

$$E(t) = \begin{cases} Nv(0,t) & \text{pre} - \text{determined} \\ \int_0^t \alpha(\theta)v(\theta,t)\mathrm{d}\theta & \text{sporadic} \end{cases} \qquad \textbf{(3)}$$

In equation (3) the function $v(\theta, t)$ is the volume of the "phantom crystal" (the crystal which would grow unlimitedly if no impingement occurs), nucleated at time θ and grown up to the instant t. If the growth is isotropic along n dimensions, and $G(t)$ is the growth rate along each dimension, this function can be written as follows:

$$v(\theta,t) = \sigma\left[\int_\theta^t G(\tau)\mathrm{d}\tau\right]^n \qquad \textbf{(4)}$$

The parameter σ accounts for crystallite shape. For spherical crystallite, the so-called *spherulite*, its value is $\sigma = 4\pi/3$.

In order to use the crystallization kinetic model described by equations (1-2) or equations (1 and 3-4), one needs experimental data for material functions tuning.

Isothermal DSC measurements are the most common way to get experimental information on Avrami exponent, m, and on semi-crystallization time, $t_{1/2}$ [8].

The more sophisticated model for expectancy, equations (3-4), requires growth rate, G, and nucleation density/rate, N or α, estimation. Many techniques have been developed and used, and most of them have been mentioned in the review by Eder and Janeschitz-Kriegl [7]. Such experiments, however, are not so simple to be carried out as the DSC measurements are. With reference to the isotactic polypropylene, a method to tune the non-lumped model starting from DSC measurements is described in the following. Most part of the work in the present paper has been carried out on an iPP resin (T30G) gently supplied by Montell.

Growth rate, G, can be described by the following equation, obtained from Lauritzen and Hoffmann theory [4]:

$$G = G_0 \exp\left[-\frac{U^*}{R\left(T - T_g + T_\infty\right)}\right]\exp\left[-\frac{\kappa_G (T_m)^2 (T_m + T)}{2T^2 (T_m - T)}\right] \qquad \textbf{(5)}$$

In order to use equation 5 the crystal melting temperature, T_m, and the polymer glass transition temperature, T_g, have to be known. Furthermore, four distinct parameters have to be estimated: G_0, U^*, T_∞ and κ_G (the parameters tuning procedure will be discussed in **Results and discussion** section).

Eder and Janeschitz-Kriegl ([7], fig. 5.23, page 303) report a collection of growth rate data for the α-phase of isotactic polypropylene. These data have been collected by different Authors, and they are reported here as open symbols in Figure 1. These Authors worked with different resins (iPPs) and different methods. However, in a G versus T plane all data appear nicely arranged along a single curve. Some experimental determination of growth rate, carried out on the resin subject of this work (iPP T30G) are also reported in Figure 1 as close diamonds [9], and they compare well with the other data. On the basis of these data, on could assume that a single set of parameters can be inserted in equation 5 to describe the growth rate data of Figure 1 for *any* isotactic polypropylene, when crystallization takes place giving the α-phase.

The semi-crystallization time can be modeled in analogy to the growth rate, i.e. by an extension of Lauritzen and Hoffmann theory [8]:

$$\frac{1}{t_{1/2}}=\left(\frac{1}{t_{1/2}}\right)_0 \exp\left[-\frac{U^*}{R\left(T-T_g+T_\infty\right)}\right]\exp\left[-\frac{\kappa_t\left(T_m\right)^2\left(T_m+T\right)}{2T^2\left(T_m-T\right)}\right] \qquad \textbf{(6)}$$

Once the parameters of equation 5 have been identified, only two additional parameters have to be determined in eq. 6: $(1/t_{1/2})_0$ and κ_t. For the resin object of this work (iPP T30G), Figure 2 reports the semi-crystallization data obtained from DSC measurements carried out in the frame of a different work [10]. An Avrami exponent $m = 3$ was also obtained in this last work, and it has been interpreted in term of three-dimensional growth starting from pre-determined nuclei, that is the common behavior of the isotactic polypropylene.

Once the growth rate, G, and the semi-crystallization time, $1/t_{1/2}$, are known and the pre-determined nucleation followed by three-dimensional growth ($m = n = 3$, $\sigma = 4\pi/3$) has been selected as the crystallization mechanism, the nuclei density, N, can be estimated. Solving the first of equation (3) and comparing with equation (2) one obtains:

$$k=\frac{\ln(2)}{t_{1/2}^3}=\frac{4\pi}{3}NG^3 \qquad \textbf{(7)}$$

From equation 7 the nuclei density can be easily obtained:

$$N=\frac{3}{4\pi}\ln(2)\left(\frac{1/t_{1/2}}{G}\right)^3=\left\{\frac{3}{4\pi}\ln(2)\left[\frac{\left(1/t_{1/2}\right)_0}{G_0}\right]^3\right\}\exp\left[-3\frac{\left(\kappa_t-\kappa_G\right)T_m^2\left(T_m+T\right)}{2T^2\left(T_m-T\right)}\right] \qquad \textbf{(8)}$$

Equation 8 allows the nuclei density estimation, starting from the knowledge of growth rate (that has been identified to be unique for any isotactic polypropylene) and from the measurement of semi-crystallization time (that can be obtained by DSC). Equation 8 predicts bell-shaped behavior of the nuclei density with temperature. The nuclei density is zero in correspondence of melting temperature, T_m, and when (absolute) temperature is zero itself. The maximum is expected at $\left(\sqrt{5}-1\right)T_m/2$.

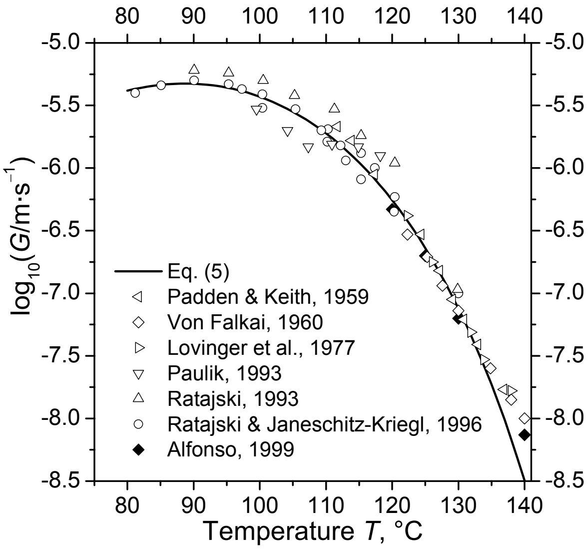

Figure 1 – Experimental and calculated growth rate data. The open symbols are data from various Authors obtained by several methods with different iPP resins, as reported by Eder and Janeschitz-Kriegl [7]; the closed diamonds (♦) are data measured [9] on the resin subject of this study (iPP T30G); the curve is calculated by equation (5) using parameters from table 1, run S3

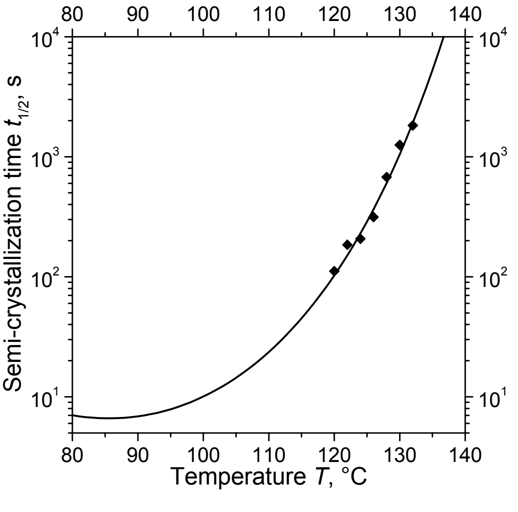

Figure 2 – Experimental and calculated semi-crystallization time data. The closed diamonds (♦) are data measured [9] on the resin subject of this study (iPP T30G); the curve is calculated by equation (6) using parameters from table 1, run S3

3. Results and discussions

Subject of this section is the identification of a set of parameters suitable to describe the isothermal crystallization of the studied iPP. The steps of the method adopted are described in details (§ 3.1), and the results, in term of nuclei density, are discussed (§ 3.2).

3.1 Growth rate and semi-crystallization time fitting

The first step is to tune the growth model, equation 5, on the basis of the data reported in Figure 1. In the present analysis, the iPP glass transition temperature is selected to be $T_g = 263.15$ K (–10°C) and the equilibrium melting temperature is selected to be $T_m = 467.15$ K (194°C). The fitting procedure can be performed by varying the four parameters $\{G_0, U^*, T_\infty, \kappa_G\}$ or only some of them. In particular, it is common to take the values for $\{U^*, T_\infty\}$ from literature. In the fundamental work by Lauritzen and Hoffmann [4] they start from $U^*/R = 2068.8$ K ($U^* = 17200$ J/mol·K = 4110 cal/mol·K) and $T_\infty = 51.6$ K, that are the values used in WLF equation for prediction of viscosity dependence upon temperature. On the basis of purely fitting arguments, they found a better agreement of experimental data with equation 5 for some materials (isotactic polystyrene, nylon 6, poly(tetramethyl-*p*-silphenylene siloxane):TMPS) when values of $U^*/R = 755$ K ($U^* = 6280$ J/mol·K = 1500 cal/ mol·K) and $T_\infty = 30$ K are used in fitting. More recently, the same values of U^* and T_∞ have been adopted in describing growth rate of isotactic polypropylene [11]. However, over all these experimentation the range of undercooling investigated is limited (at last 60 K for iPP, [11]), and this strongly limits the applicability of the fitted parameters, as the Authors themselves stated at the beginning of the fitting procedure ([4], par. 4.2, page 566). The fitting can be reconsidered since Eder and Janeschitz-Kriegl reported iPP growth data for larger undercooling (more than 100 K) [7].

In the present work four distinct fitting strategies have been adopted, and results are summarized in Table 1. In the first attempt, code S1, the values of U^*/R and T_∞ came from conclusions of Lauritzen and Hoffmann, and growth data fitting gives only the values of G_0 and κ_G. In simulation S2 the value for U^*/R has been changed adopting the early value of 2068.8 K, and in simulation S3 also the value for T_∞ has been changed to the early value of 51.6 K. All the fitted sets of parameters allow equation 5 to describe the growth data of Figure 1, but only the last attempt (S3) captures the correct behavior, with a maximum in correspondence of 80°C (353.15 K). The simulation S4, carried out by taking all the four parameters as variable during fitting, does not further improve the data description. It is worth noticing that the fitting procedure is greatly simplified once the parameters (U^*/R and T_∞) have been selected. In fact, the data can be reported in the Lauritzen and Hoffmann plane, $[\log(G) + U^*/(2.303\cdot R(T-T_g+T_\infty))]$ versus $[T_m^2(T_m+T)/(2.303\cdot 2\cdot T^2(T_m-T))]$. In this plane, the data become linear, the fitting line has the intercept equal to $\log(G_0)$ and the slope equal to κ_G.

Table 1. Optimization strategies for growth rate (eq. 5) and semi-crystallization time (eq. 6) fitting (the parameters used in regression are typed in italic in gray background cells).

Simulation Code	T_∞	U^*/R	G_0	κ_G	$(1/t_{1/2})_0$	κ_t
	K	K	m/s	dimensionless	1/s	dimensionless
S1	30.0	755.0	*$1.53\cdot10^{3}$*	*2.0303*	*$4.13\cdot10^{8}$*	*2.3487*
S2	30.0	2068.8	*$4.4\cdot10^{9}$*	*2.7757*	*$1.13\cdot10^{15}$*	*3.0885*
S3	51.6	2068.8	*$4.36\cdot10^{8}$*	*2.7979*	*$1.74\cdot10^{14}$*	*3.1710*
S4	*56.5*	*2067.1*	*$3.64\cdot10^{7}$*	*2.4474*	*$9.46\cdot10^{12}$*	*2.7621*

In conclusion, the data of Figure 1 can be correctly described by equation 5 and the parameters obtained in the frame of fitting attempt noted as S3. The values of U^*/R = 2068.8 K and T_∞ = 51.6 K seems to be more correct in describing the growth rate of α-phase iPP. Of course, this result is connected with the data available, and it is realistic as well as the data themselves are correct.

The fitting procedure has been extended to the semi-crystallization data of Figure 2, described by equation 6, obtaining values for $\{(1/t_{1/2})_0, \kappa_t\}$ (following the linear fitting procedure described above, with the exception of simulation S4). The description of the data is satisfactory for all the set of parameters in Table 1. Obviously, the set correspondent to attempt S3 (used in growth data description) has been selected for the subsequent work, and the prediction of equation 6 with these parameters is reported in Figure 2.

If one wants to apply the procedure depicted until now to another iPP, the growth rate has to be described by equation 5 with the values of $\{G_0, U^*, T_\infty, \kappa_G\}$ from Table 1, simulation S3 (the couple {equation + parameters} should applies to any α-phase iPP). The semi-crystallization data for the studied polymer have to be determined experimentally (e.g. by DSC), and equation 6 has to be fitted to these data, adopting the same value of $\{U^*, T_\infty\}$ and determining the values for $\{(1/t_{1/2})_0, \kappa_t\}$.

3.2 Nuclei density evaluation

Figure 3 reports some nuclei density data, measured on the resin subject of this work [9], together with a linear fitting function. In the limited temperature range investigated, the fitting by the power law is very accurate. However, the power law has to be intended as a "dangerous" way to describe the nuclei density, useful only if adopted in the same temperature range in which it has been tuned. Very low temperatures, inserted in fitting equation, give up to very high, and unrealistic, nuclei density values.

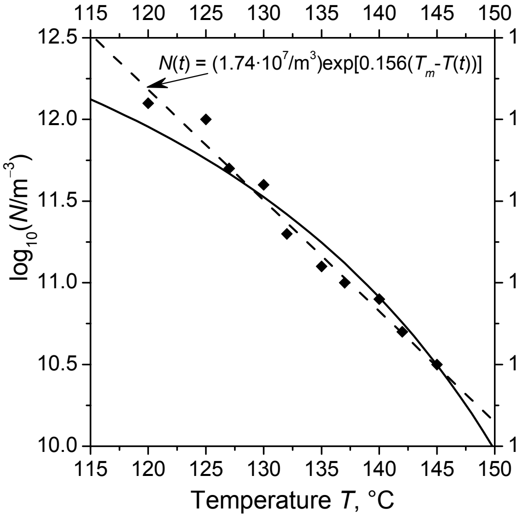

Figure 3 – Experimental and calculated nuclei density data. The closed diamonds (♦) are data measured [9] on the resin subject of this study (iPP T30G); the continuous curve is calculated by equation (8) using parameters from table 1, S3

The alternative way to predict the nuclei density proposed in the present work is equation 8. Once growth rate and semi-crystallization time has been tuned, equation 8 does not include any further optimization parameter. On the basis of the parameter obtained in optimization S3 (Table 1, discussed in previous section), the prediction of equation 8 is reported in Figure 3 as a continuous curve. The agreement with experimental data is very good (without any further optimization), and, in addition, the general behavior of equation 8 is more realistic than the behavior of linear fit.

4. Conclusions

In this work, growth rate and semi-crystallization time data for iPP α-phase, taken from literature, have been used as a basis to tune the Lauritzen and Hoffmann equation. The nuclei density has been derived and compared favorably with some experimental data. The procedure followed is extremely easy, it does not require cumbersome multi-parameters fitting work and needs only some DSC measurements. It is described in detail and it could be applied to any polypropylene with very little amount of experimental work.

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