Crystallization and Microstructure in Quenched Slabs of Various Molecular Weight Polypropylenes: Modified Modeling and Experiments

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ABSTRACT: The purpose of the present work was to bring further improvements to the simulation of the crystallization process in terms of morphology and crystallinity in quenched slabs of isotactic polypropylenes (i-PP). Incorporation of the temperature dependence of specific heat, density, and thermal conductivity into a previous simulation program based on their constant values does not influence the predicted results. A new approach to calculate the nuclei concentration to obtain the gapwise distribution of spherulite diameter was proposed and tested. A microthermocouple was placed in the PP slabs to follow the crystallization process during their quenching. The temperature traces as a function of time were measured. With this technique, it was possible to determine the correct heat transfer coefficient and the induction time for crystallization at high cooling rates relevant to injection molding. The present results indicate an importance of the decrease of the heat release during crystallization at high cooling rates. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2003–2015, 1999

INTRODUCTION

Injection molding is one of the most important polymer processing operations in the plastic industry. The simulation of the process is very important to cut down the expensive tooling costs and to improve the final quality of the product by predicting the physical properties of the molded part. The filling stage of the process is now well predicted, and the new efforts have been concentrated in the improvement of the post-filling stages, packing and cooling.^{1–5} In the injection molding of semicrystalline polymers, the most important aspect is the development of the microstructure model. New attempts are required to describe, as closely as possible, the crystallinity and morphologies developed in the process because of their influence on the final proper-

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ties of the molding. Recently, the shear-induced crystallization was incorporated into the simulation of injection molding, and the prediction of the skin layer was made.^{1,2} Furthermore, for the first time, a comparison is made between the predicted and experimental data on the gapwise distribution of spherulite diameter in quenched slabs with the purpose to develop a model for the injection molding simulation.⁶ The reported results showed only qualitative agreement with experimental data. As a continuation of this previous work, the present article incorporates the temperature dependence of physical properties and modified nucleation concept with the purpose of improving the description of the experimental results.

EXPERIMENTAL

Materials and Methods of Investigation

Three grades of isotactic polypropylenes (i-PP) were used in the quenching experiments. These grades include Profax PP6823, PP6723, and

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Polymer	MFI (dg/min)	PI	M_w	
PP6823	0.51	3.9	670,000	
PP6723 PP6523	$\begin{array}{c} 0.92 \\ 4.1 \end{array}$	$\begin{array}{c} 3.9\\ 4.3\end{array}$	557,000 351,000	
PP6523	4.1	4.3	351,0	

Table IMaterial Properties Providedby Himont

PP6523, provided by Himont USA, Inc. They are simply different melt flow grades of homopolymer polypropylene with a general purpose stabilization package. Material properties are given in the Table I.

Compression molding was used to prepare 200 μ m thick sheets and discs of various thicknesses and 25.0 mm in diameter, respectively. A 75- μ m iron-constantan thermocouple was sandwiched between two sample discs or sheets, and an aluminum foil was wrapped around circumference to keep the samples and the thermocouple together. The thermocouple was connected to a PC with a data acquisition system to record the temperature profile as a function of time. The sample was placed in an oven at 200°C and annealed for about 15 min. Then it was guenched in water at 25°C or in air at 25°C. The temperature profile as a function of time for the heating process and for quenching was recorded. After quenching, the sample was cut, and the actual thickness and thermocouple position in the gapwise direction were determined using a Leitz 12 Pol S Optical Microscope with a calibrated scale. This information was used in the simulation of the temperature profile and the size of spherulites. The gapwise distribution of spherulite diameters was measured using the microscope described above. For this purpose, microtome cuts of approximately 20 μ m were made in the thickness direction in the samples quenched in air. The cuts were made using microtome Leico. For water at 25°C, the simulated results were compared to the experimental data obtained in the previous work by Isayev and Catignani.⁶

All the data required for the simulation, such as the radial growth rate, nonisothermal rate constant, heat of crystallization, ultimate degree of crystallinity, induction time, and others were taken from the previous work.⁶

Theoretical

Quiescent Crystallization Kinetics

The Avrami equation $^{7-9}$ has been largely used to describe the overall crystallization process during

isothermal conditions. Assuming a fixed-temperature, independent value for the number of initially present nuclei per unit volume, it takes the following form:

$$\theta(t) = 1 - \exp\{-\mathbf{k}(\mathbf{T})t^n\}$$
(1)

where $\theta(t)$ is the fraction of crystallized material after the time t at the isothermal crystallization temperature T. k(T) is the isothermal rate constant, and n is the Avrami exponent.

The half-time of conversion $t_{1/2}$ can be obtained from eq. (1) and takes the following form:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{2}$$

During actual processing conditions, the crystallization takes place under nonisothermal conditions. So, numerous attempts^{10–12} have been made to extend the theory to nonisothermal conditions. The most accepted and used model was proposed by Nakamura et al.¹¹ On the basis of isokinetic conditions, which assume the same temperature dependence for the radial growth rate *G* and the crystallization rate constant k(T), Nakamura obtained the following model:

$$\theta(t) = 1 - \exp\left[\left(\int_0^t \mathbf{K}(\mathbf{T})(t')\right) dt'\right)^n \qquad (3)$$

where $\theta(t)$ is the relative degree of crystallinity at the time *t* and K(T) is the nonisothermal crystallization rate constant. The differential form of the Nakamura equation is more useful for processing simulation and takes the form

$$\frac{d\theta}{dt} = n \operatorname{K}(\mathrm{T})(1-\theta) [-\ln(1-\theta)]^{(n-1)/n} \qquad (4)$$

The nonisothermal rate constant is related to the isothermal one through the following equation proposed by Nakamura et al.¹¹:

$$\mathbf{K}(\mathbf{T}) = [\mathbf{k}(\mathbf{T})]^{1/n} = \frac{(\ln 2)^{1/n}}{t_{1/2}}$$
(5)

Using the Hoffman et al.¹³ equation for the overall rate of isothermal crystallization, $1/t_{1/2}$, and eq. (5), the temperature dependence of the nonisothermal rate constant may be expressed as

$$\mathbf{K}(\mathbf{T}) = (\ln 2)^{1/n} \left(\frac{1}{t_{1/2}}\right)_0 \exp\left(\frac{-U^*/\mathbf{R}}{T - T_{\infty}}\right) \exp\left(\frac{-K_g}{T\Delta Tf}\right)$$
(6)

where

$$\Delta T = T_m^0 - T ext{ and } f = rac{2T}{T+T_m^0}$$

where R is the universal gas constant, T_m^0 is the equilibrium melting point, and f is a correction factor for the dependence of the latent heat of fusion with the temperature. $(1/t_{1/2})_0$ is a preexponential factor that includes all terms independent of the temperature, U^* is the activation energy for the segmental jump rate, K_g is the nucleation exponent, and T_∞ is taken as the glass transition temperature minus 30°C.

Although the Nakamura model is largely used for simulation of the crystallization during processing conditions, new models are being proposed and tested because the whole crystallization process still cannot be described with the desired precision. Recently, Isayev and Catignani⁶ compared the Nakamura model to a general Avrami's model of impingement and Tobin's model of impingement using the approach proposed by Schneider et al.^{14–15} The simulated results showed that the gapwise distribution of spherulite diameters are very similar for these three models.⁶ So, in the present work, the Nakamura model for nonisothermal crystallization was used.

The Nakamura equation does not take into account an induction time for the crystallization process. The method proposed by Sifleet et al.¹⁶ is used to calculate the nonisothermal induction time by summation of isothermal induction times according to

$$\bar{t} = \int_0^{t_l} \frac{dt}{t_i(T)} = 1 \tag{7}$$

where t_i is the isothermal induction time, t_I is the nonisothermal induction time, and \bar{t} is the induction time index. When this index reaches unity, the quiescent crystallization begins. For melt crystallization, the isothermal induction time is assumed to follow the Godovsky and Slonimsky¹⁷ equation, as follows:

$$t_i = t_m (T_m^0 - T)^{-a}$$
 (8)

where t_m and a are material constants independent of temperature and are obtained normally by differential scanning calorimetry (DSC) experiments. Combining eqs. (7) and (8) and integrating under constant cooling rate conditions, the nonisothermal induction time assumes the following particular form:

$$t_I = \left[\frac{t_m(a+1)}{b^a}\right]^{1/(a+1)}$$
 (8b)

where b is the cooling rate and $T = T_m^0 - bt$.

To calculate the gapwise distribution of spherulite diameters, the nuclei concentration is necessary. Assuming instantaneous nucleation for three-dimensional spherulite growth, the nuclei concentration takes the following form¹⁸:

$$N(T) = \frac{3V_{\infty}\mathbf{k}(T)}{4\pi G(T)^3}$$
(9)

where V_{∞} is the maximum volume fraction of spherulites at $t \to \infty$, G is the radial growth rate, and k(T) is the isothermal Avrami rate constant. The spherulite diameter is assumed to be equal to L, the average distance between nuclei. For instantaneous three-dimensional spherulitic growth, L takes the following form^{14,15}:

$$L = \left(\frac{V_{\infty}}{8\,\pi\bar{N}}\right)^{1/3} \tag{10}$$

where \bar{N} is the nuclei concentration. In the previous work, ${}^6\bar{N}$ was assumed to be equal to $N(T_i)$, where $T_i = T(t_i)$ is the temperature when the induction time index reaches unity and the crystallization begins. In the present work, a new method to calculate \bar{N} was introduced. In this case, \bar{N} is not a function only of the first temperature when the crystallization begins but an average for the whole crystallization process based on the remaining amorphous fraction because new nuclei can be formed only in this phase. Mathematically, it can be expressed by

$$\bar{N} = \int_0^1 N(T)(1-\theta) \ d\theta \tag{11}$$

where N(T) is given by eq. (9).

After the crystallization process is finished in a given gapwise location, the calculated \bar{N} value is

used to obtain the average spherulite diameter for that location by using eq. (10).

Crystallization and Morphology in Quenched Slabs

The simulation of the quenching process was performed by using the Fortran program developed in the previous work⁶ modified to include nonconstant physical properties as a function of temperature and the new equation to calculate the average nuclei concentration described above. This program is based on the one-dimensional equation of heat conduction incorporating the heat of crystallization and can be written as

$$\rho C_p \frac{\partial T}{\partial t} = k_{th} \frac{\partial^2 T}{\partial z^2} + \rho \Delta H_c X_{\infty} \frac{\partial \theta}{\partial t}$$
(12)

where ρ , C_p , and k_{th} are the density, specific heat, and thermal conductivity of the material; T is the temperature at time t at a distance z from the center of the sample in the thickness direction, ΔH_c is the heat of crystallization for pure crystal; X_{∞} is the ultimate crystallinity; and $\partial \theta / \partial t$ is the crystallization rate. The initial conditions are

$$T(0, z) = T_i, \ \theta(0, z) = 0 \ \text{at} \ t = 0$$

where T_i is the initial temperature of the molten polymer. The boundary conditions are

$$\frac{\partial T}{\partial t} = 0 \text{ at } z = 0$$

and

$$-k_{th} \frac{\partial T}{\partial z} = h(T - T_q)$$

or

$$rac{\partial T}{\partial z} = -rac{Bi}{H}\left(T-T_q
ight)$$

at z = H, where $Bi = hH/k_{th}$ is the Biot number, H is the half thickness of the sample, T_q is the quench temperature, and h is the heat transfer coefficient between the sample and the quench medium. The rate of crystallization is given by eq. (4).



Figure 1 Thermal conductivity, 20 specific heat, 20 and density 2,19 as a function of temperature for i-PP based on data in the literature.

RESULTS AND DISCUSSION

Effect of Thermal Properties

As mentioned before, the first attempt was made in the present work to obtain simulated results in terms of the gapwise distribution of spherulite diameter closer to the experimental ones by the incorporation of the temperature dependence of physical properties. The data was taken from literature for the density,^{2,19} specific heat,²⁰ and thermal conductivity.²⁰ Figure 1 shows the fitted curve for the specific volume as a function of temperature, as obtained in Isayev et al.,² based on the experimental data from Hieber and Chiang.¹⁹ Also, Figure 1 shows the reproduction of the fitted curves obtained in Wang et al.²⁰ for specific heat and thermal conductivity. Figure 2 shows the comparison of the new simulated gapwise spherulite diameter distribution for nonconstant physical properties to the simulated ones obtained in the previous work.⁶ It can be seen that the influence of the nonconstant properties on the simulated results is very small. Therefore, it cannot explain the difference between the simulated and the experimental values shown in Isayev and Catignani.6

Figure 3 shows the comparison of the simulated temperature traces at the center of the sample and at a position close to the wall during quenching in water at 25°C. It can be observed from Figure 3 that the simulated temperature traces at a position close to the wall are practically the same. At the center, the difference is more pronounced, but only in terms of some shifting the curve along the time axis and not chang-



Figure 2 Comparison of the simulated gapwise spherulite diameter distribution for PP6723 slab of thickness 2H = 3.3 mm quenched in water at 25° C using constant and nonconstant physical properties.

ing the shape of the curve. This kind of influence practically does not have any effect on the size of the spherulite because, according to the model, it depends on the temperature when the crystallization begins. This temperature is practically the same for constant and nonconstant physical properties. Similar results were obtained for quenching in air at 25°C. So, due to the desire of using a model as simple as possible to describe the process, the constant physical properties program is used further in the present work. In this case, the following values for the physical properties were used⁶: $\rho = 900 \text{ Kg/m}^3$; $C_p = 2140 \text{ J/(kgK)}$; and k = 0.193 W/(mK).

Another possibility that could be used to explain the discrepancy between the experimental and the simulated results is V_{∞} , the maximum volume fraction of spherulites at $t \to \infty$. This parameter is usually considered constant, but it could be a function of the cooling rate. For the thick sample (3.3 mm), as can be seen in the Figure 3, the predicted temperature traces at the center and at the point close to the wall are different. For the thin sample, it would be practically the same. If the values of V_{∞} were a function of the cooling rate, different values should be used in eqs. (9) and (10), and different gapwise distributions of spherulite diameter could be obtained. However, according to the present model, the size of spherulites given by L does not depend on the

 V_{∞} because it is canceled in the eqs. (9) and (10). So, even if this parameter were a function of the cooling rate, it would not change the calculated spherulite diameter.

According to eqs. (9) and (10), the size of spherulite depends on the nuclei concentration. The nuclei concentration depends on the G and kparameters that are strongly temperature-dependent.⁶ The temperature profile depends on the heat transfer coefficient for the quenching medium h. In the previous work,⁶ the value of h was a fitting parameter based on the comparison of the experimental and simulated gapwise distribution of spherulite diameters. However, different values of h caused only a shifting of the curve along the diameter axis instead of changing the shape and slope, as is necessary to describe the experimental results.⁶ So we concluded that it would be very important to get information about the actual temperature trace as a function of time. This was done by using a microthermocouple inserted in the sample during the quenching experiments. Figure 4 shows a typical heating process for the sample placed in the oven for melting and annealing before quenching. It can be seen that upon melting, the rate of temperature rise decreases; and after fusion is completed, it increases again until the temperature reaches 200°C.



Figure 3 Comparison of the simulated temperature traces at the center and at a position close to the wall in the PP6723 slab of thickness 2H = 3.3 mm quenched in water at 25°C using constant and nonconstant physical properties.



Figure 4 Typical temperature traces during heating process for the i-PP slabs of initial thickness 2H = 3.1 mm placed in the oven for melting and annealing before quenching.

Measured and Calculated Temperature Traces

Figure 5(a) shows measured and calculated temperature traces during the quenching process for the PP6723 in water at 25°C. It can be observed that when the crystallization takes place, the temperature traces show different slopes due to the associated heat release. Using the measured temperature at specified thermocouple positions for this sample, the heat transfer coefficient was obtained by fitting the simulated curve to the experimental one during the early stage of quenching. The value obtained for h is 350 $W/(Km^2)$, which is higher than the highest one used in the previous work, 250 W/(Km²).⁶ However, it is seen that the simulated curve shows a maximum that is not seen in the experimental one, indicating that the whole quenching process is not predicted well in this case. The maximum in the simulated curve could indicate that the heat release is being overpredicted. The value for the ultimate degree of crystallinity, X_{∞} and the corresponding heat release Q_f were obtained using DSC experiments at a cooling rate of 2.5 C/min.⁶ They are shown in Table II. These values are being used to simulate the quenching process. However, the crystallinity obtained after quenching in water was lower than the ultimate degree of crystallinity observed at 2.5 C/min due to the higher cooling rates.⁶ For the PP6723 and PP6823 shown in Figure 5(a) and (b), respectively, and

quenched in water at 25°C, the crystallinity developed corresponds to approximately 83 and 85% of the ultimate value.⁶ The degree of crystallinity developed after quenching was obtained by DSC



Figure 5 (a) Measured and simulated temperature traces at Y/H = 0.01 during quenching of PP6723 slab of thickness of 2H = 3.28 mm in water at 25°C. Curves (1) and (2) correspond to the initially amorphous and crystalline sample, respectively. (b) Measured and simulated temperature traces at Y/H = 0.14 during quenching of PP6823 slab of thickness 2H = 3.61 mm in water at 25°C. Curves (1) and (2) correspond to initially amorphous and crystalline sample, respectively.

Table II Heat Release Q_{β} Ultimate Degree of Crystallinity X_{∞} Obtained in DSC at 2.5°C/min Cooling Rate and Relative Degree of Crystallinity θ_{∞} Developed During Quenching in Water at 25°C⁶

Sample	$Q_{f}\left(\mathrm{J/g} ight)$	X_{∞}	$ heta_{\infty}$
6523	110.56	0.529	0.71
6723	93.10	0.4598	0.83
6823	91.02	0.4355	0.85

at a heating rate of 10°C/min using the area under the melting peak minus the area under the crystallization peak (which is zero for PP) divided by the total heat for fully crystallized sample. Since the T_g for PP is lower than the room temperature, it is possible that some crystallization took place after the quenching but before the DSC experiments were carried out. However, the degree of crystallinity by the DSC cannot be measured immediately after quenching. About 30 min is required to cut the specimen from a quenched slab and to microtome it for the DSC measurements. The degree of crystallinity measured by the DSC at various times up to 24 h after quenching did not show any variation with time after quenching. At the same time, in order to shift the simulated curve for the temperature trace closer to the experimental one, the heat release used for the simulation of the temperature trace during quenching should be even lower than 83% of its ultimate value. Figures 5(a) and (b) present the influence of the heat release on the simulated temperature curves for 100, 83, 60, and 40% of crystallinity based on the ultimate heat release Q_{f} . It is seen that the calculated temperature curves and maximum are progressively decreased with the decrease of the final degree of crystallinity utilized in calculations. Also, calculated curves come progressively closer to the experimental curve, indicating a possibility that the degree of crystallinity immediately after quenching is lower than that measured by DSC.

Evidently, part of the discrepancy between the simulated and experimental temperature traces shown in Figures 5(a) and (b) can be attributed to the heat release. However, there is another possible reason for this discrepancy, as evidenced from calculations and measurements of temperatures during quenching of the initially crystallized sample in water at 25°C from 140°C. As seen from Figures 5(a) and (b), for temperatures below 90°C, the simulated curves without heat release,

Q = 0.0, show a slower decrease of temperature than expected. Around 60°C, the predicted values become higher than the experimental values obtained during quenching of the initially amorphous sample at 200°C. The incorporation of the nonconstant physical properties, not shown in these figures, did not change this trend. In the simulation, a constant value for the heat transfer coefficient h was used. However, it is possible that the value of h is not constant during the whole quenching process since water undergoes a phase transition at 100°C. The value of h should be higher at low temperatures to explain the difference between the simulated and experimental results. Finally, it should be mentioned that discrepancy between simulated and experimental temperature profiles arises only when the crystallization is completed. Therefore, this discrepancy should not affect the simulation of the size of spherulites.

One of the biggest problems in simulating the crystallization during actual processing conditions is the lack of experimental techniques to obtain all the model parameters in a wide range of temperatures or high cooling rate observed during processing. Much work has been done to overcome this deficiency by using, for example, the master curve approach²¹ for determining the nonisothermal crystallization rate function. Recently, Ding and Spruiell²² used a special device based on light depolarizing microscopy to measure the growth rate G at high cooling rates and low temperatures as observed in processing conditions. In addition to these parameters, the induction time function, eq. (8), needs to be obtained. In the previous work,⁶ the induction constants a and t_m were obtained by fitting the DSC data for cooling rates up to 40°C/min (the DSC loses the control at higher cooling rates). Then, they were used to predict the beginning of the crystallization during the quenching, where average cooling rates are about one order of magnitude higher. Therefore, it is not clear if the discrepancy between the predicted and the measured size of the spherulites in Isayev and Catignani⁶ is due to the model simplicity or extrapolation of induction time model to high cooling rates. To clarify this situation, the quenching was performed at conditions where the model parameters determined earlier⁶ are much more reliable. This was done by quenching the samples in air where the average cooling rates (around 60°C/ min) are closer to those used to get the model parameters.



Figure 6 Measured (curve 1) and simulated (curves 2, 3, and 4) temperature traces during quenching of i-PP slabs in air at 25°C. PP6523: Y/H = 0.65, H = 1.335 mm, h = 24 W/(m²K), and $Q_f = 110.56$ J/g; PP6723: Y/H = 0.18, H = 1.44 mm, h = 27 W/(m²K), and $Q_f = 93.10$ J/g; PP6823: Y/H = 0.04, H = 1.775 mm, h = 27 W/(m²K), and $Q_f = 91.02$ J/g.

Figure 6 presents the temperature traces as a function of time for PP6523, PP6723, and PP6823 cooled in air from 200 to 25°C. It can be seen that the simulated curves for PP6523 and PP6723 are closer to the experimental ones than those for quenching in water. The maximum shown by the predicted curves can now be observed in the experimental curves too, except for the PP6523 sample, where the thermocouple was closer to the wall than in the other samples. The presence of a maximum means that the rate of heat release due to the crystallization is faster than the ability of the quenching medium to take the heat from the sample. When they are the same, a flat portion in the curve is observed. If the rate that the heat is taken away from the sample is faster than the heat being released, the slope of the curve will be negative, even in the presence of crystallization. One reason for the smaller difference between the simulated and experimental curves for cooling in air than that observed in water is the value of the heat release used. It was observed that the degree of crystallinity obtained by the DSC for these samples are approximately the same for cooling rates between 2.5 and 40°C/min.⁶ So, probably, the crystallinity developed during the cooling in air is closer to the ultimate degree of crystallinity

 X_{∞} obtained in the DSC. The cooling process during the quenching in water is much faster than that in the air. Therefore, information obtained using the DSC cannot be easily applied to processes in which fast cooling rates take place.

It is seen in Figure 6 that the simulated temperature decay for the three samples during the cooling in air after the crystallization is completed is slower than the corresponding experimentally observed. These results are similar to those depicted in Figures 5(a) and (b) obtained for quenching in water. The simulated curves for Q= 0.0 J/g still cross over the experimental ones at low temperatures, although for the PP6823 sample, it occurs later. It indicates that even for air the heat transfer coefficient possibly is not constant for the whole cooling process. However, the use of a constant value of h will not affect the prediction of the distribution of the size of the spherulites because the discrepancy occurs after the crystallization is completed.

Spherulite Size in Quenched Slabs

As mentioned before, the value for the heat transfer coefficient used in the previous work was a fitting parameter based on the gapwise distribution of the spherulite diameter.⁶ The values used were in the range between 62.5 and 250 W/(Km²). Since the value of h determined experimentally during the quenching in water in the present work is higher than the highest value used in,⁶ the simulation was performed using a new value of h. The results are compared with the experimental results obtained previously.⁶ The average nuclei concentration according to eq. (11) was also used to obtain the spherulite diameter. Figures 7(a)-(c) show the comparisons between the simulated and experimental gapwise distribution of the spherulite diameters for PP6523, PP6723, and PP6823 samples quenched in water at 25°C. These figures show that the simulated gapwise distributions of the diameter based on the earlier method⁶ to obtain the nuclei concentration, N= $N(t_i)$, and based on the old a and t_m parameters can predict the experimental results only in a narrow region close to the sample wall. However, in the center, the simulated values are much smaller than the experimental ones. It can be observed that the integral eq. (11) for obtaining the nuclei concentration N provides a gapwise distribution of the diameters closer to the experimental ones. The predicted diameters at the center are much larger than the ones obtained using the nuclei concentration according to the earlier



Figure 7 (a) Measured⁶ and simulated spherulite diameters for PP6523 quenched in water at 25°C: 2H = 3.3 mm, $h = 350 \text{ W/(m^2K)}$, and $Q_f = 110.56 \text{ J/g}$. (b) Measured⁶ and simulated spherulite diameters for PP6723 quenched in water at 25°C: 2H = 3.3 mm, $h = 350 \text{ W/(m^2K)}$, and $Q_f = 96.10 \text{ J/g}$. (c) Measured⁶ and simulated diameters for PP6823 quenched in water at 25°C: 2H = 3.3 mm, $h = 350 \text{ W/(m^2K)}$, and $Q_f = 96.10 \text{ J/g}$. (c) Measured⁶ and simulated diameters for PP6823 quenched in water at 25°C: 2H = 3.3 mm, $h = 350 \text{ W/(m^2K)}$, and $Q_f = 91.02 \text{ J/g}$.

method, although it is still lower than the experimental ones. At the wall, the integral form of \bar{N} provides spherulites with diameters lower than \bar{N} obtained from the induction time, $\bar{N} = N(t_i)$, but closer to the experimental values. However, at Y/H = 0.5 to 0.9, the simulated spherulite size

obtained using the integral form of \overline{N} are strongly underpredicted. Moreover, from Figures 7(a)–(c), one can see the influence of the heat release on the spherulite diameters. It was shown in Figures 5(a) and (b) that the simulated temperature traces using the crystallinity obtained for sam-



Figure 8 (a) Measured and simulated spherulite diameters for PP6523 cooled in air at 25°C: 2H = 2.4 mm, $h = 24 \text{ W/(m}^2\text{K})$, and $Q = Q_f = 110.56 \text{ J/g}$. (b) Measured and simulated spherulite diameters for PP6723 cooled in air at 25°C: 2H = 2.88 mm, $h = 27 \text{ W/(m}^2\text{K})$, and $Q = Q_f = 96.10 \text{ J/g}$. (c) Measured and simulated spherulite diameters for PP6823 cooled in air at 25°C: 2H = 3.0 mm, $h = 27 \text{ W/(m}^2\text{K})$, and $Q = Q_f = 91.02 \text{ J/g}$.

ples quenched in water are closer to the experimental ones than those obtained using the ultimate degree of crystallinity X_{∞} from the DSC experiments. In contrast, Figures 7(a)–(c) show that the use of the corrected heat release provides the gapwise spherulite diameter distributions lower than those obtained for the heat release associated to the ultimate degree of crystallinity.

Figures 8(a)–(c) show the comparisons between the simulated and the experimental spherulite diameters for the samples quenched in air. It can be observed that the results based on $\overline{N} = N(t_i)$ cannot predict the experimental data. However, for the PP6523 sample, the results for the integral form of N are very close to the experimental gapwise distribution of the diameters. The corresponding simulated diameters for the PP6723 sample are also close to the experimental values; but for the PP6823 sample, the predicted results are good only for positions near the wall. These results indicate that the model using the integral eq. (11) for obtaining the average nuclei concentration for the whole crystallization process provides reasonable prediction of the size of spherulites for samples quenched in air. Therefore, the unsatisfactory results obtained for quenching in water could be, at least in part, a consequence of the extrapolation used for obtaining some model parameters at high cooling rates or low temperatures. As seen from the temperature traces for samples quenched in water and air, at the beginning of the crystallization process, the simulated curves go under the experimental ones. It indicates that the predicted induction times are longer than the actual ones, and some correction is needed.

Quenching experiments using very thin samples with the microthermocouple inserted can give more reliable information about the induction time at high cooling rates. Thin samples of about 400 μ m were used. In these samples, the temperature is almost the same along the thickness and the beginning of the crystallization is more easily determined. When thin samples are used, the cooling rates are high, even for samples cooled in air, as shown in Figure 9 for PP6523, PP6723, and PP6823 samples. Equations (7) and (8) were used with the a and t_m parameters determined from the DSC data⁶ for cooling rates up to 40°C/min to calculate the induction times for these experimental curves. The calculated results are compared to the experimental induction times determined based on times where the slope significantly decreases. It is observed that the predicted values are always larger than the experimental ones, especially for the PP6823 sample, where the calculated t_i seems to be located at the completion of the crystallization. This fact can



Figure 9 Experimental temperature traces with predicted and measured induction times for i-PP samples of thickness 2H = 0.4 mm cooled in air at 25°C. Predicted induction times are based on old parameters.

explain why the simulated temperature profiles for this sample quenched in water and air [Figures 5(b) and 6] lie below the experimental ones when the crystallization takes place. The PP6723 sample shows the best prediction for t_i . This explains why simulated and experimental temperature curves for quenching in water, [Fig. 5(a)] and in air [Fig. 6] are close to each other at the beginning of the crystallization.

Induction Time

The comparisons between the predicted and experimental t_i shows that the parameters a and t_m in eq. (8) need to be recalculated to provide a better description of the experimental temperature trace during quenching. New values for a and t_m were obtained by refitting eq. (7) to experimental induction times from the DSC data⁶ and from the quenching experiments in air for thick and thin samples, as shown in Figures 6 and 9,

Table III Old⁶ and New a and t_m Parameters for Induction Time Model

Sample	Old a	$Old \ t_m \ (sK^a)$	New a	New $t_m (sK^a)$
PP6823 PP6723 PP6523	10 10 10	$egin{array}{llllllllllllllllllllllllllllllllllll$	$11.125 \\ 11.50 \\ 9.75$	$egin{array}{c} 1.004 imes 10^{21} \ 1.009 imes 10^{21} \ 1.450 imes 10^{18} \end{array}$



Figure 10 Measured and simulated temperature traces during quenching of PP6823 slabs of thickness 2H = 3.61 mm in water at 25°C. $Q = Q_f = 91.02$ J/g.

respectively. The values of a and t_m are shown in Table III. Figure 6 also shows the comparison between the experimental temperature traces and the simulated curves using new values of a and t_m for the thick samples. The use of the corrected parameters provides simulated and experimental curves close to each other at the beginning of the crystallization. However, this improvement is clear only for the PP6823 sample quenched in air and water, as shown in Figures 6 and 10, respectively. At the later stage of crystallization, the predicted curves for the two values of a and t_m become close. It shows that the induction time parameters have more effect at the early stage of crystallization.

Figures 7(a)-(c) present the influence of the new parameters a and \boldsymbol{t}_{m} on the simulated gapwise distribution of the diameters. It is seen that the new simulated diameters are larger than those obtained for the previous values of a and t_m .⁶ This is a consequence of shorter induction times and higher crystallization temperatures. However, it is seen that the simulated diameters based on $N = N(t_i)$ are more influenced by the new values of a and $t_{\rm m}$ than those from the integral equation. This happens because, in the first case, the nucleation density is based only on the temperature corresponding to the induction time, while in the last case, the nuclei concentration is an average for the whole crystallization process. As shown in Figures 6 and 10, different induction

time parameters have more effect on the beginning of the crystallization but do not affect so much the process after crystallization is completed. It also shows that the simulated diameters based on $N = N(t_i)$ are much more sensitive to any uncertainty in the determination of the induction time function than those obtained from the integral method.

Figure 11 presents a comparison of the nonisothermal induction time as a function of cooling rate for new and old a and $t_{\rm m}$ parameters. The calculated values were obtained by using eq. 8(b). This figure also shows the experimental induction time from the DSC data⁶ and from the quenching experiments. In this last case, an average cooling rate calculated from T_m^0 until the beginning of the crystallization was used to plot the corresponding induction time. It is seen that the new fitted curves present induction times shorter than the previous ones, especially for high cooling rates. This new fitted curve can better describe the experimental data from DSC and from quenching for the PP6723 sample. It shows that the method proposed by Sifleet et al.¹⁶ given by eq. (7) associated with the isothermal induction time proposed by Godovsky and Slonimsky¹⁷ is good for predicting the nonisothermal induction time in a wide range of cooling conditions. However, for the PP6823 sample, the experimental induction times obtained from the quenching experiments are shorter than the predicted ones. This explains why the simulated temperature traces for this sample using new a and t_m for the samples quenched in air and water shown in Figures 6 and 10, respectively, still go under the experimental ones.

CONCLUSION

A simulation approach developed in a previous work⁶ was modified to incorporate nonconstant physical properties and a new method to calculate the nuclei concentration used to obtain the gapwise distribution of spherulites diameters for quenched samples. A microthermocouple was used to follow the crystallization during the quenching experiments. This technique is very simple and inexpensive but provides very important information in the evaluation of simulation programs for describing the crystallization process of semicrystalline polymers during processing conditions. It eliminates the problem with the temperature lag that occurs when nonisothermal experiments are performed without measuring



Figure 11 Nonisothermal induction time as a function of cooling rate: (1) PP6523; (2) PP6723; (3) PP6823. The calculated curves were obtained from eq. (8b). The induction times from quenching were plotted against the average cooling rate.

the actual sample temperature, especially for high cooling rates. With this technique, the correct heat transfer coefficients for quenching the PP slabs in various media were determined, and the induction times for the beginning of crystallization at high cooling rates were obtained. These values were used to recalculate the a and $t_{\rm m}$ parameters that are used to predict the induction time.

It was shown that the use of nonconstant physical properties does not significantly change the simulated results. Also, it does not explain the discrepancy between the predicted and experimental spherulite diameters observed in the previous work.⁶ The integral equation for calculating the nuclei concentration leads to better description of the experimental spherulite diameters than the earlier method based on the instantaneous induction time. This equation is less sensitive to any uncertainty in the determination of the induction time function.

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