RESEARCH ARTICLE

ScienceAsia 27 (2001) : **127-132**

Mathematical Modeling of Solidification of Semi-crystalline Polymers under Quiescent Non-isothermal Crystallization: Determination of Crystallite's Size

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Received 28 Sep 1999
Accepted 26 Jan 2001

ABSTRACT In this paper, a mathematical model for the solidification of the semi-crystalline polymers is proposed to predict the size of the crystallites. In addition to the degree of the crystallinity, the size of the crystallites is one of the structural variables, which can shape the mechanical properties of the polymer materials. During the quiescent non-isothermal processes, the mean radius of crystallites is a function of both nucleation and growth process. The density of the potential nuclei is assumed to follow the nucleation law. With the stochastic approach, the nucleation centers and the activation temperatures are randomly assigned to these potential nuclei. A radial front-tracking method is used to determine the evolution of the shapes of crystallites, according to the dependence of the growth rate on the temperature. In a realistic study of solidifying High Density Polyethylene, the simulation results allow us to predict the mean size of the crystallites at the various cooling rates.

KEYWORDS: solidification, crystallite size, crystallinity, non-isothermal crystallization, differential scanning calorimetry

INTRODUCTION

In addition to the degree of the crystallinity, the size of the crystallites is one of the structural variables, which can shape the mechanical properties of semi-crystalline polymers. Polymer melts that exhibit irregularity in the molecular chain can form crystalline structures during cooling. The growth of spherulites can be usually observed by the polarized-light microscope when cooling from the melt. In the studies of Janeschitz-kriegl,[1] cross-sections through polypropylene samples were observed after running the DSC experiment at different cooling rates of 5 and 50°C/min. It was found that the average size of the spherulites is much smaller with the higher cooling condition. The small size of the spherulites gives good mechanical properties while the polymer materials are brittle when they have large spherulites. Sharples[2] also reported that yield stress in Nylon 66 varies according to the size of the spherulite. It was observed that the yield stress increases when the mean size of spherulites decreases. Hence, it is important to qualitatively determine the final crystallite size of the polymer materials under any arbitrary cooling conditions in polymer processing.

However, the quantitative mechanisms of the spherulite's development remain unclear. There have been a few researches to study the shape evolution of a spherulite in various thermal conditions.[3-7] In the approach of Schulze and Naujeck,[3-4] the shape of a spherulite is analytically determined by any points that are reached by the growing fibrils from the nucleation center itself. Lovinger and Gryte[5] implemented the thermal conditions and the dependence of the growth rate on the temperature in the thermal fields. The directions of the shape evolution depend on the thermal gradient and follow Snell's Law of light diffraction due to the growth-rate changes with the temperature. However, this method is limited due to the difficulties of the numerical computation of the front directions when the thermal gradients are large. Swaminarayan and Charbon[6-7] proposed two methods, that is, the arborescent method and the front-tracking method in order to avoid such drawbacks. In the Arborescent method, the growth of the spherulites is modeled by following individual fibrils of which branching can be made in all possible orientations. Although applicable to all thermal conditions, this method requires large computation time and memory. Compared to the Arborescent method, the front-tracking method yields simulation results faster and requires less computation memory. This method is based on the assumption that the fronts of the spherulites will grow normally outward with a growth rate given by the local temperature at that moment. In this study, the front-tracking method is used to simulate the growth of the individual spherulites. With the stochastic approach for the nucleation, the resulting simulations of the shape evolutions are obtained to predict the mean sizes of the spherulites on the various cooling conditions

MATERIAL AND EXPERIMENT

The High Density Polyethylene (HDPE) was obtained from Thai Petrochemical Industry Public Co, Ltd Its commercial designation is Polene V1160. For a determination of the glass temperature, dynamic mechanical analysis was used by running Perkin Elmer DMA 7series. The temperature of the HDPE sample was increased from -140°C to 0°C with heating rate 5°C/min by using Helium purge gas at 20 cm^3/min. For Differential Scanning Calorimetry DSC, the experiments of the non-isothermal conditions considered in this study were performed by Leephakpreeda[8], which yielded the parameters of the crystallization kinetics embedded Artificial Neural Model (ANM) and the non-isothermal induction time model as discussed in Appendix A.

NUCLEATION AND GROWTH KINETICS

In a theoretical treatment, a quiescent crystallization is thought to proceed by the number of the nuclei being formed randomly in the polymer melts. The number of the initial nuclei per unit volume or so-called nucleus density n depends on the temperature and supercooling. The nucleation of semi-crystalline polymers is typically hetero-geneous, which implies that the nucleation depends not only on the thermal history but also on the purity of the melt. Hence, it is difficult to apply the theoretical models of the nucleation. In an empirical approach, Icenogle[9] proposed a nucleation law representing the simple linear relationship between the nucleus density and the temperature:

$$n(T)=n_0\left(1-\frac{T}{T_0}\right) \qquad 0<T<T_0 \qquad (1)$$

where n_0 and T_0 are material constants, which can be determined by the thermal analysis of DSC. These tiny nuclei, which already exist in the liquid phase can be activated at any time. As soon as they are activated and stable, they become the growing crystallites. This entity grows in all the available directions until it impinges on another entity. At this moment, the growth of both entities stops at the impingement point. The usual feature of crystallite is the spherulite, which is an aggregate of crystallite plate-like lamellae. Assuming that a potential nucleus starts growing at a given time t_0, the distance r which the front of the crystallite transverses during time increment $d\tau$ with the linear growth rate $\dot{G}$, after it has grown to time T, is:

$$r=\int_{t0}^{t}\dot{G}(T(\tau))d\tau \qquad (2)$$

where T is the local temperature of the semi-crystalline polymer.

The growth rate has been analyzed theoretically and the dependence of the growth rate on the temperature T is basically given by[10]

$$\dot{G}(T)=\dot{G}_0 e^{-\left(\frac{E_D}{RT}\right)} e^{-\left(\frac{F}{kT}\right)} \qquad (3)$$

where E_D is the activation energy for the transport process at the interface, F is the free energy of the formation of a surface nucleus of a critical size, k is Boltzmann's constant and $\dot{G}_0$ is a pre-exponential term which is not dependent on the temperature.

Van Krevelen[10] has derived a universal correlation for the linear growth rate over the temperature range between the glass temperature T_g and the equilibrium melting temperature T_m^0. Using the following definitions: $\overline{T}=(T_m^0+T_g)/2, K=T_m^0/T$ and $\varsigma=T_g/T_m^0$, the expression for the growth rate is for $T>\overline{T}$:

$$\dot{G}(T)=\dot{G}_0 e^{-5.3\left(\frac{K}{1-\varsigma}\right)} e^{-264.8\left(\frac{K^2}{T_m^0(K-1)}\right)}$$

and for $T<<\overline{T}$

$$\dot{G}(T)=\dot{G}_0 e^{-\frac{2060.8K}{51.63K+T_m^0(1-K\varsigma)}} e^{-264.8\left(\frac{K^2}{T_m^0(K-1)}\right)} \qquad (4)$$

where $\dot{G}_0$ is normally taken as 10^{12} nm/sec for PE and typical polymers.

As mentioned earlier, the interface between the spherulite and the melt grows normal to itself with the growth rate given by the local temperature as expressed in Eq (4). However, it is possible to attenuate the computation burden by following the radial directions instead. The normal growth rate, given by Eq (4), can be converted into the radial growth rate:

$$\dot{G}_r = \dot{G}\Big/\sqrt{1+(r'/r)^2} \qquad (5)$$

with

$$r' = \frac{dr}{d\theta} \qquad (6)$$

where r and θ are the space variables in the r-θ coordinate system.

In the simulations, the radial directions are evenly spaced at the nucleation center. The locations of the interface along those directions are then determined by numerically integrating Eq (2) in the time steps. The contour of the spherulite can be obtained by connecting the points on the interface for any given time.

Simulation Results and Discussion

For the nucleation, the initial number of the potential nuclei is determined by the nucleation law in Eq (1). The parameters of the model of the nucleation law used in this simulation are taken from Icenogle[9] for the crystallization of PE. It can be written as:

$$n^{(3D)}(T) = 5.89\times10^{12}\left(1-\frac{T}{401}\right) \qquad (7)$$

where $n^{(3D)}$ is the three dimensional spherulite density (m^{-3}) and T is the crystallization temperature (K).

Note that the crystallization temperature is defined as the temperature that has the highest rate of crystallization kinetics during the process. The prefactor of three dimensional spherulite density in Eq (7) can be converted to one of the two dimensional spherulite density by using the stereological relationship[7]:

$$n_0^{(2D)} = 1.458\left(n_0^{(3D)}\right)^{2/3} \qquad (8)$$

where $n_0^{(2D)}$ is the prefactor of the two dimensional spherulite density.

With Eqs (7) and (8), the two dimensional spherulite density can be obtained as:

$$n^{(2D)}(T) = 4.76\times10^{8}\left(1-\frac{T}{401}\right) \qquad (9)$$

where $n_0^{(2D)}$ is the two dimensional spherulite density (m^{-2})

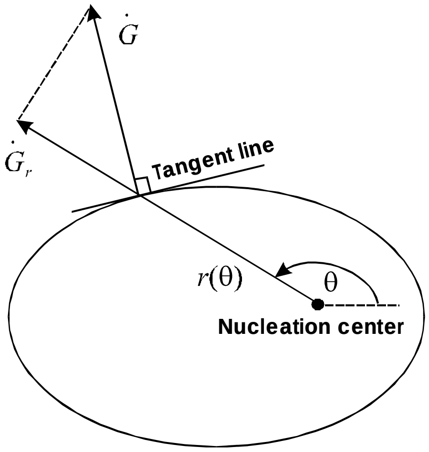


Fig 1. Geometric diagram of the relation between the normal growth rate $\dot{G}$ and the radial growth rate $\dot{G}_r$.

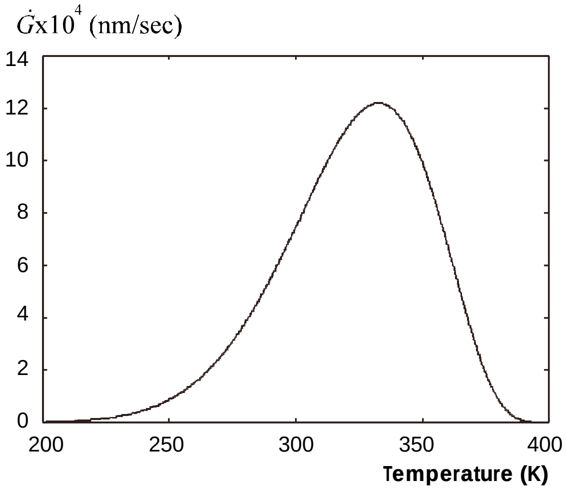


Fig 2. Growth rate of the spherulites as the function of the crystallization temperature.

Eq 9 is used as the nucleation law to estimate the number of potential nuclei per unit area. In the simulations, the potential nuclei of $n^{(2D)} A$ are randomly distributed at positions within the surface area of the sample A. The temperatures, when the nuclei are activated, are randomly assigned to each of the nuclei within a range of the crystallization temperature. The higher the activation temperature, the sooner the nucleus is activated. In the case where two nuclei are located at the same position, the nuclei with the lower activation temperature is absorbed by the growing crystallite with the higher activation temperature. This is equivalent to the assumption that if a potential nucleus is overlapped by a spherulite before its activation, it will never be activated. The temperature profile within the sample is required to determine whether nuclei are activated and to then track the fronts of the evolving spherulites. To determine the temperature dependence of the growth rate in Eq (4), the glass transition temperature of the HDPE sample is experimentally determined to be -87.62°C. Fig 2 shows the plot of the linear growth rate versus the temperature.

For the cases of simulations, consider the three different cooling processes in DSC runs with constant rates, that is 0.5, 10 and 75°C/min respectively. The cooling rates of 0.5, 10 and 75°C/min are chosen to represent the quiescent non-isothermal crystallization at low, medium and high cooling rates respectively. Let's assume that the uniform temperature takes place within polymer sample during DSC experiments. In Fig 3, the evolution of the crystallinity is determined from the crystallization kinetics embedded ANM and the non-isothermal induction time model in Appendix A. The crystallization temperature can then be obtained as shown in Table 1. As the cooling rate increases, the crystallization temperature occurs at a lower temperature. According to Eq (9), the number of the potential nuclei per unit area proportionally increases.

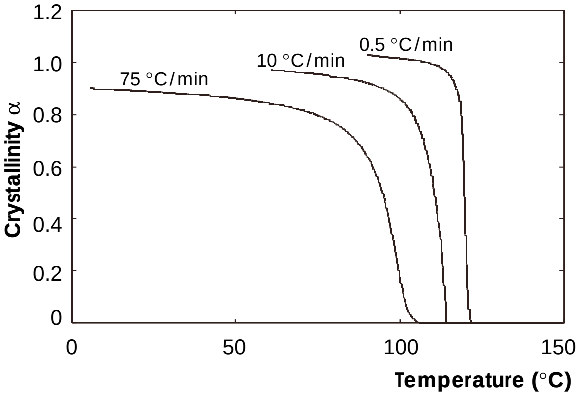


Fig 3. Prediction of the evolution of the crystallinity at cooling rates 0.5, 10 and 75 °C/min.

Table 1. Crystallization temperatures and the corresponding numbers of the potential nuclei at various cooling rates.

Cooling rate (°C/min)	Crystallization temperature (°C)	Number of nuclei (m^{-2})
0.5	119.6	$10\text{x}10^6$
10	107.4	$24\text{x}10^6$
75	94.4	$40\text{x}10^6$

Consequently, more potential nuclei, which are nucleated at higher cooling rates, have possibilities to become growing crystallites. This explanation agrees with the resulting simulations of the complete evolution of the morphology in Fig 4. At cooling rates 0.5, 10 and 75°C/min , the number of spherulites per unit area are found to be 3, 6 and 8 mm^{-2} respectively. According to Fig. 4, the number of the spherulites per unit area increases at higher cooling rate. On the other hand, the mean of the maximum size of spherulties increases at lower cooling rate as illustrated in Table 2 and is determined by the following equation:

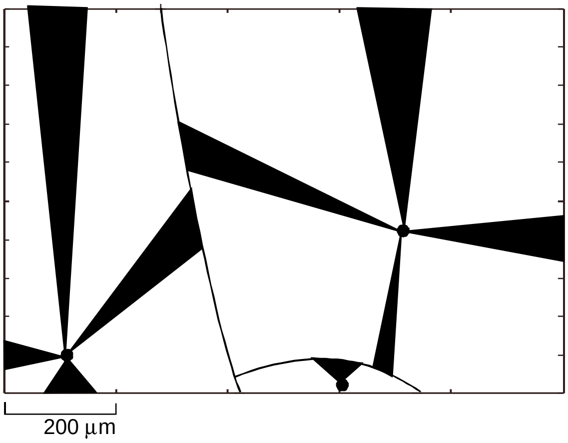
$$\bar{r}_{\max} = \left(\frac{A}{N\pi}\right)^{1/2} \tag{10}$$

where A is the area of the simulated sample and N is the number of the spherulites.

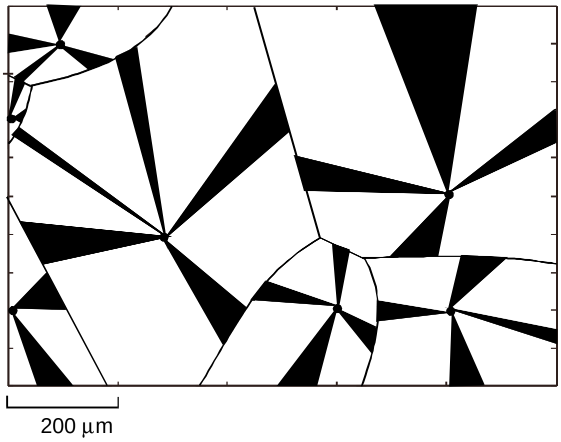
Table 2. The mean of the maximum size of the spherulites at various cooling rates.

Cooling rate (°C/min)	Spherulite size $\bar{r}_{\max}$ (μm)
0.5	325
10.0	230
75.0	199

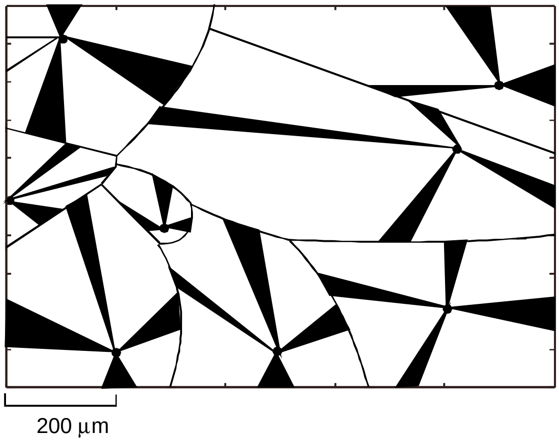
These results can be explained by the fact that the more the population of spherulites or nuclei, the less their occupied areas, in the other word, the smaller the radius of the spherulites. Therefore, this implies that the mean of the spherulite size can be influenced by the simultaneous interaction between



(a) Morphology at cooling rate 0.5 ° C/min



(b) Morphology at cooling rate 10 ° C/min



(c) Morphology at cooling rate 75 ° C/min

Fig 4. Predictive simulations of the morphology of the HDPE sample at cooling rates 0.5°C/min (4a), 10°C/min (4b) and 75°C/min (4c).

nucleation and growth which are dependent on the cooling conditions. The cooling rate thus has a great effect on the kinetics of crystallization and the formation of the microstructure. At high cooling rate, the spherulites form a fine structure. If cooling is slower, a few nuclei form and the resulting spherulites become coarser.

CONCLUSIONS

The mathematical model proposed in this paper has been used to simulate the solidification of the semi-crystalline polymers under quiescent non-isothermal conditions. The resulting simulations of a microscopic polymer part have provided not only the shape of the spherulites but also their size. The viability of the proposed methodology can be showed by a realistic non-isothermal case study of cooling HDPE in DSC at various cooling-rate conditions.

APPENDIX

The model of crystallization kinetics embedded Artificial Neural Model (ANM) of Leephakpreeda[8], is reviewed in order to quantitatively describe the crystallization process under the quiescent non-isothermal conditions. The evolution of the crystallinity α can be described by Eq. (A1).

$$\alpha(t)=\int_{t_{cs}}^{t}\left(\frac{d\alpha}{d\tau}\right)_{ANM} d\tau \qquad \text{(A1)}$$

where t_{cs} is the starting time of the crystallization, $d\alpha/dt$ is the rate of the crystallization kinetics, and t is the time.

Fig A1 illustrates the rate of the crystallization kinetics, which is a function of the temperature and the crystallinity. It should be noted that the values of the rate of the crystallization kinetics in section A

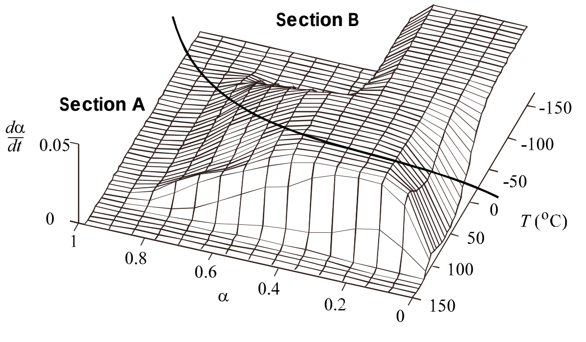


Fig A1. The rate of the crystallization kinetics generated by ANM.

were interpolated from DSC data of the same bulk of the HDPE in this study while the ones in section B were extrapolated due to no available data. However, the resulting simulations of the crystallinity were obtained from using the values of the rate of the crystallization kinetics in the section A.

In order to determine when the crystallization actually starts, that is t_{cs}, the induction time model is to be considered. After the polymers are cooled below the equilibrium melting temperature, the delay time that is required for the nucleation process is called the induction time. For the melt-crystallization, the isothermal induction time is assumed to follow Eq. (A2).

$$t_i = t_m (T_m^0 - T)^{-\gamma} \tag{A2}$$

where t_m and γ are the material constants independent of temperature and T_m^0 is the equilibrium melting temperature.

The non-isothermal induction time t_I can be obtained from the isothermal induction time.

$$\bar{t} = \int_0^{t_1} \frac{1}{t_i} d\tau = 1 \tag{A3}$$

where is the dimensionless induction time index

The value of equilibrium melting temperature is 143 °C. The values of γ and t_m are equal to 8.19 and $2.13\text{x}10^{13}$ respectively for HDPE.

ACKNOWLEDGMENTS

This research was financially supported by a grant from National Science and Technology Development Agency (NSTDA), Thailand.

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