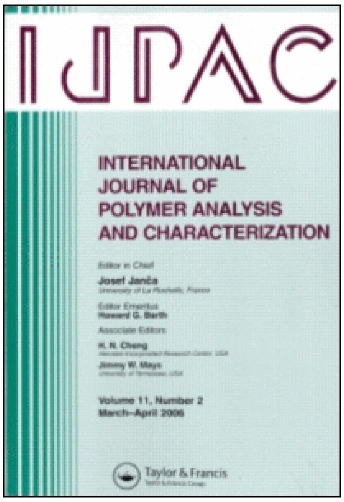

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Crystallization Kinetics Study of Polyethylene

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Abstract: Crystallization kinetics of polyethylene was studied using differential scanning calorimetry. Isothermal crystallization kinetics was analyzed using the Avrami equation. Non-isothermal crystallization kinetics was analyzed using different models, namely, the Avrami, Jeziorny, Ozawa, Nakamura, Dietz, and Kamal-Chu models. The advantages and disadvantages of these models are outlined based on comparison between experimental and modeling results.

Keywords: Crystallization kinetics; Polyethylene

INTRODUCTION

It is important to understand the crystallization behavior of polymers from both academic and industry perspectives. The properties of a crystalline polymer, like the thermodynamic, spectroscopic, physical, and mechanical, depend on the details of crystal structure and crystal morphology that develop from the melt. Understanding the crystallization mechanism is a key to understanding these properties.

The crystallization of polymers is usually considered as a transformation consisting of three stages: nucleation, growth of crystals, and secondary crystallization. Nucleation is the process by which a crystalline nucleus is formed at melt state. After the nucleus is formed, a new layer grows on the surface of the existing one. The crystallization completes with the process called secondary crystallization, which gives an increase

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of crystallinity and thickness of already formed lamellar crystals. The study is generally conducted under isothermal condition, since the use of a constant temperature permits an easier theoretical treatment and limits the problems connected with thermal gradients within the samples. However, the analysis of non-isothermal crystallization is also of great importance, since it is more closely related to polymer processing conditions. Moreover, it may expand the general understanding of the crystallization behavior of polymers, since the isothermal methods are often restricted to narrow temperature ranges. Several techniques, such as the dilatometric, microscopic, spectroscopic, and calorimetric, have been used to study crystallization kinetics.

Numerous studies have been reported on crystallization of polymers, and many models have been proposed to describe isothermal and non-isothermal crystallization.[1–10] Avrami[1] first developed an equation for describing isothermal crystallization. Ziabicki[2] suggested that non-isothermal crystallization can be regarded as a sequence of isothermal steps. The proposed equation was a series expansion of the Avrami equation. Ozawa[3] proposed a model for the process of nucleation and subsequent growth under constant cooling rate by modifying the Avrami equation. Nakamura et al.[4,5] derived a model based on the presumption that the kinetics of primary nucleation and of crystal growth rate is similar so that the ratio of growth rate to nucleation rate is constant (isokinetic conditions). Patel et al.[6] later suggested a differential form of the Nakamura model. Dietz[7] also proposed a kinetic equation for non-isothermal crystallization with consideration of secondary crystallization. More recently, Ziabicki[8,9] and Ziabicki and Sajkiewicz[10] presented a new model where transient thermal and athermal effects were included.

As we can see from the above, there has been a long history in developing these models. Different assumptions and methods were used by different researchers for different polymers. It would be an advantage to test these models using the same polymer under the same conditions. The purpose of this article is thus to investigate the validity of these models. Comparison and comments on them will also be given.

EXPERIMENTAL SECTION

Material

The polyethylene was from Equistar Chemical Company. The resin has a melt index of 0.95. The weight average molar mass is 141,529 g/mol and polydispersity index (M_w/M_n) is 7.6. The density is 0.958 g/cm^3. The melting temperature is 133.0°C and the crystallinity is 0.705, which was measured using differential scanning calorimetry (DSC).

DSC Experiment

Crystallization kinetics was studied using a Perkin-Elmer DSC-7, which was calibrated with indium. Nitrogen gas was purged during scanning. The sample weight was approximately 5 mg to minimize temperature gradient inside the sample. For the isothermal crystallization experiment, the samples were first melted at 180°C for 5 min to eliminate the previous thermal history and then quickly cooled to the designated temperature. For the non-isothermal crystallization experiment, the samples were cooled to 25°C at various rates (1, 10, 20, 30, 40, 50, 60, 70, and 80°C/min).

RESULTS AND DISCUSSION

Isothermal Crystallization Kinetics Study

Figures 1(a) and (c) show heat flow and relative crystallinity development for isothermal crystallization at various temperatures. It can be seen that polyethylene melt crystallizes very quickly and there is no induction time. When $\mathrm{Tc} \leq 117^\circ\mathrm{C}$, the crystallization proceeds so rapidly that a considerable amount of crystallinity is produced during cooling. Therefore, the isothermal analysis is performed at every 1°C in the interval of 117–122°C.

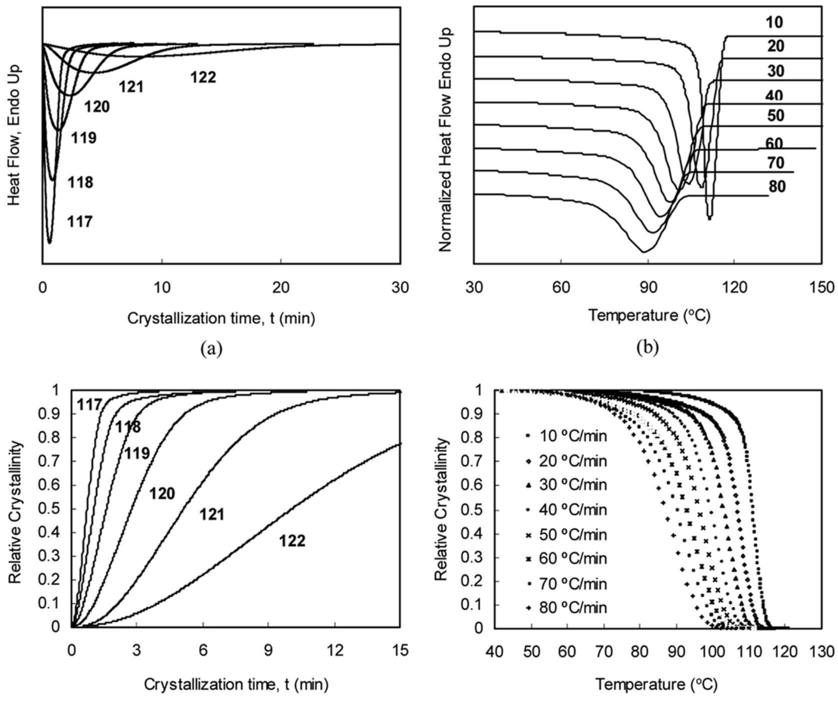
The isothermal crystallization kinetics is usually interpreted using the Avrami equation,[1] based on three assumptions: (1) isothermal transition conditions; (2) random nucleation; (3) growth rate of a new phase dependent only on temperature and not on time (linear growth rate). The general form of the Avrami equation is:

$$1 - X_t = \exp(-Kt^n) \tag{1}$$

where X_t is the relative amount of crystallinity at time t, K is the crystallization rate constant, and n is the Avrami exponent. K and n can be determined by:

$$\log[-\ln(1 - X_t)] = \log K + n \log t \tag{2}$$

The Avrami index thus calculated is around 2. The fractional number may be attributed to volume changes on crystallization, incomplete crystallization, annealing, or different mechanisms involved during crystallization. It is well known that the Avrami index is related to the type of nucleation mechanism and the geometry of crystal growth. For three-dimensional crystal growths, the Avrami index will be 3 or 4 after being heterogeneously or homogeneously nucleated. Here, the Avrami index



(a) (b)

(c) (d)

Figure 1. (a) Heat flow vs. time for isothermal crystallization; (b) heat flow vs. temperature for non-isothermal crystallization; (c) relative crystallinity vs. time for isothermal crystallization; (d) relative crystallinity vs. temperature for non-isothermal crystallization.

measured is lower than the theoretical value. Janimak and Stevens[12] ascribed it to the nucleation effect in commercial polyethylene. They suspected there might be some catalyst residues or fillers, such as stabilizers and antioxidants, in the raw materials. During crystallization, these particles would act like nucleation agents, which means the Avrami index should be in the range of $1 \sim 3$. However, our thermogravimetric analysis (TGA) result shows there is no such additive in the raw materials.[11] Even if there were small amounts, the measured Avrami index is still lower than the theoretical value. Based on Cheng's theory,[13] Equation (1) can be rewritten as

$$1 - X_t = \exp(-gNv^n t^n) \tag{3}$$

for the case of predetermined nuclei. Here v is the radial growth rate, g is a geometrical factor (which is $4\pi/3$ for spheres), and N represents the number of nuclei per unit area. If v is characterized to be a linear rate of crystal growth, Equation (3) is now equivalent to Equation (1) with $K = gNv^n$. However, if v is not a constant radial growth rate, but can be expressed in the form of

$$v = v_0 t^m \tag{4}$$

Equation (3) must thus be cast into

$$\log[-\ln(1 - X_t)] = \log g + \log N + n \log v_0 + n(m+1)\log t = \log K^* + n(m+1)\log t \tag{5}$$

where $K^* = gNv_0^n$ and $n(m+1)$ is called an *apparent coefficient*. For a diffusion-controlled transition, the growth rate would scale as $t^{-0.5}$. According to Equation (5), the apparent coefficient becomes $0.5n$, and it would be 0.5, 1, and 1.5 for one-, two-, and three-dimensional growths, respectively. In general, the exponential number of Equation (4), m, is smaller than zero if the radial growth rate slows down with respect to time ($m = 0$ when v is a linear growth rate). The apparent coefficient in this case is, therefore, always smaller than the dimensionality n expressed in Equation (1) for a linear crystal growth rate.

In the kinetics studied here, a possible reason for $m < 0$ and, thus, a lower apparent coefficient n may be the restriction of the crystal growth due to previously formed crystals, therefore reducing molecular mobility. The change of n with respect to temperature must be attributed to a combination of several rate-determination steps. If the crystallization temperature is high enough, one may expect only nucleation (aggregation) as the rate-determining step, and the value of n must be close to 3.

Non-isothermal Crystallization Kinetics Study

Figures 1(b) and (d) show non-isothermal crystallization and relative crystallinity development of polyethylene under different cooling rates. As the cooling rate increases, the crystallization temperature shifts to a lower temperature, which implies that crystallization happens at a lower temperature under faster cooling rate.

Application of Jeziorny Model

Jeziorny[14] used the Avrami equation to describe non-isothermal crystallization by assuming that crystallization occurs under constant temperature. After using the same procedure as in the isothermal crystallization case, the non-isothermal crystallization rate constant (K_c) can be further calculated by:

$$\log K_c = \frac{\log K}{dT/dt} \tag{6}$$

However, we found that the calculated n depend significantly on crystallization onset temperature T_o. For T_o values of 118.5°, 117.6°, and 116.8°C, the n values are 4.2, 3.2, and 2.4. A difference of only 1°C will change the Avrami index by 1. The mechanism thus inferred from the Avrami index will be totally different. We can imagine how much error will be introduced for crystallization occurring under a higher cooling rate, since the temperature will be read at a bigger space by the instrument. The n and K_c values thus obtained are not reliable.

Application of Ozawa Model

Ozawa[3] extended the Avrami equation to the non-isothermal situation, assuming that the polymer is heated or cooled at a constant rate and the mathematical derivation of Evans[15] is valid. According to the Ozawa theory, the degree of conversion at temperature T amounts to:

$$1 - X(T) = \exp(-K(T)/\gamma^n) \tag{7}$$

where $K(T)$ is the crystallization rate constant, n is the Ozawa index or Avrami exponent, and γ is the cooling rate.

To obtain n and $K(T)$, Equation (7) is rewritten as:

$$\ln[-\ln(1 - X(T))] = \ln(K(T)) + n \ln \gamma^{-1} \tag{8}$$

Plotting $\ln[-\ln(1 - X(T))]$ versus $\ln \gamma^{-1}$ at a given temperature, T, a straight line may be obtained: n and $\ln(K(T))$ can be estimated from the slope and intercept of the line.

However, Figure 3(a) shows nonlinear dependence of $\ln[-\ln(1 - X(T))]$ on $\ln \gamma^{-1}$. Elder and Wlochowicz[16] ascribed this to the secondary crystallization, dependence of lamellar thickness on crystallization temperature, and variation of Avrami's exponent with crystallization temperature. Liu et al.[17] tried to solve this problem by using a so-called mixed Avrami and Ozawa model. However, this model needs to determine the crystallization onset temperature, which will cast doubt on its reliability.

Application of Nakamura Model

Nakamura et al.[4,5] extended the Avrami equation to describe non-isothermal the crystallization process based on isokinetic assumption, meaning the number of activated nuclei is considered to be independent of temperature and the nucleation rate and the growth rate have the same time dependence.

$$X = 1 - \exp\left[-\left(\int_0^t K(T)d\tau\right)^n\right] \tag{9}$$

where $K(T)$ is related to the crystallization rate constants of isothermal crystallization K through the relation $K(T) = K^{1/n}$.

The empirical formulation of K was proposed by Takayanagi and Kusumoto[18]:

$$\ln K = \ln K_0 - \frac{E_D}{RT} - \frac{CT_m}{(T_m - T)T} \tag{10}$$

where K_0 is the constant almost independent of temperature, E_D the activation energy per molecule for transporting polymer to the surface of spherulites, and C a constant with regard to the surface (two-dimensional) nucleus. The third term in the right side of the equation corresponds to the work for two-dimensional nucleus formation on the spherulite surface and has a definite influence on the temperature dependence of growth rate at higher temperature near to melting temperature. The activation energy (E_D) is one-eighth of the viscous flow activation energy (E_{vis}), which can be obtained through:

$$E_{vis} = Rd \ln \eta_T / d\left(\frac{1}{T}\right) \tag{11}$$

where η_T can be calculated from the Williams-Landau-Ferry (WLF) equation:

$$\log\frac{\eta_T}{\eta_{T_s}} = \frac{-8.86(T - T_s)}{(101.6 + T - T_s)}, \quad T_s = T_g + 50\,K \tag{12}$$

For polyethylene, $T_m{}^\circ = 413\,\text{K}$, $T_g = 233\,\text{K}$.[20] The crystallization constant is thus

$$\ln K = \ln K_0 - \frac{62T}{(T - 181.4)^2} - \frac{413C}{(413 - T)T} \tag{13}$$

In order to get $\ln K_0$ and C, we plot $\left(\ln K + 62T/(T - 181.4)^2\right)$ versus $413/(413 - T)T$ (Figure 2(a)). The constants $\ln K_0$ and C are equal to 22.936 and 471.74, respectively. The theoretical results are compared with experimental results in Figure 2(b), which shows a good match.

The modeling results are thus plotted in Figure 3(b), which shows that the model over-predicts the experimental results and gives a better prediction at lower cooling rates. The difference between maximum

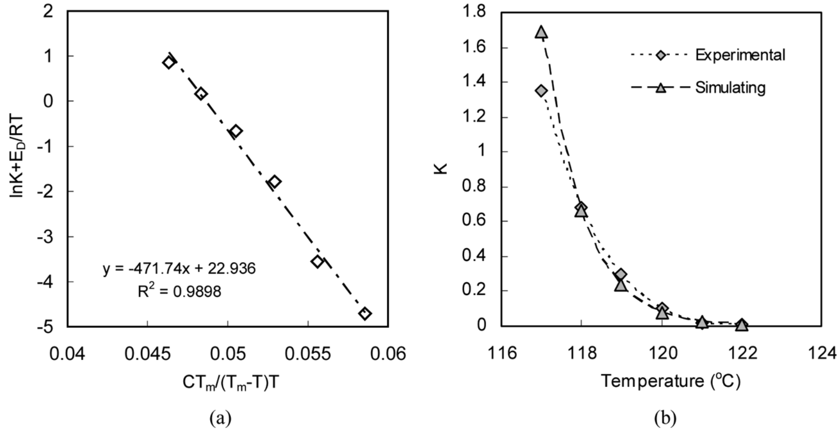


Figure 2. (a) ln $K + (E_D/RT)$ vs. $(CT_m/(T_m - T)T)$ for isothermal crystallization rate constant *K*; (b) comparison between experimental and modeling results on *K* value.

crystallization temperature of modeling and experimental results is 2°, 4°, 6°, and 10°C at 1, 10, 20, and 40°C/min. Apparently, non-isothermal crystallization at lower cooling rate resembles the isothermal crystallization condition more closely. This might be due to the model not taking into account the effect of induction time. However, polyethylene has a very fast crystallization rate, and it is impossible to measure the induction time under isothermal condition.

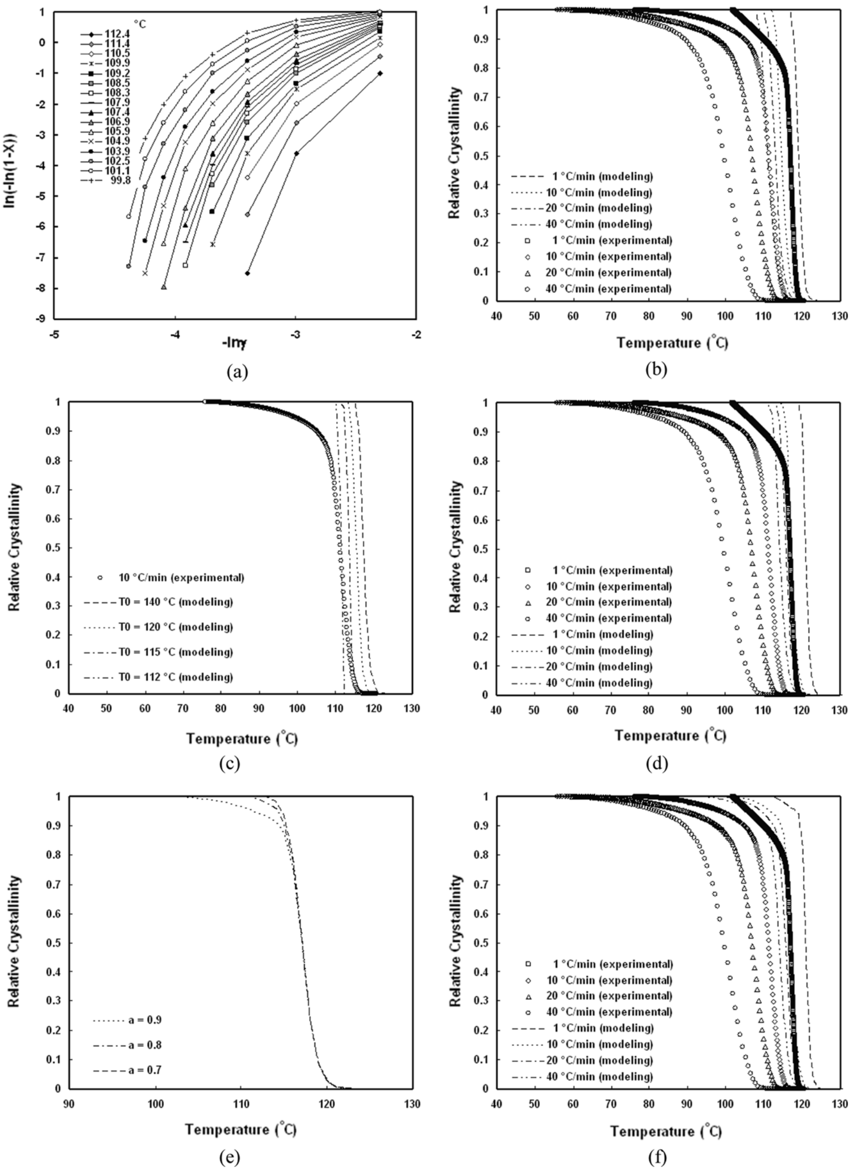
Application of Kamal-Chu Model

Based on the assumption that non-isothermal crystallization may be treated as a sequence of isothermal crystallization, Kamal and Chu[19] proposed a modified Avrami equation:

$$X = 1 - \exp\left[-\int_0^t Knt^{n-1}dt\right] \tag{14}$$

The integration was computed using $T_0 = T_m{}^\circ$ as a lower limit for the integration. K is obtained through isothermal crystallization kinetics study, as described before.

The modeling results are shown in Figure 3(d). The difference between maximum crystallization temperature of modeling and experimental results is 4°, 6°, 10°, and 15°C at 1, 10, 20, and 40°C/min. The difference is larger than that predicted with the Nakamura model. We suspect that the predicted relative crystallinity is very sensitive to the temperature from which the integral is computed and thus calculated relative crystallinity using a different starting temperature T_0 (Figure 3(c)).



(a)

(b)

(c)

(d)

(e)

(f)

Figure 3. (a) Ozawa model; (b) Nakamura model; (c) effect of T_o on Kamal-Chu model; (d) Kamal-Chu model; (e) effect of *a* value on Dietz model; (f) Dietz model.

Apparently, when using a lower start temperature, the modeling curve moves close to experimental results.

Application of Dietz Model

This model[7] introduces an additional term to consider secondary crystallization (post-Avrami). The new parameter, a, can take values within 0–1. When there is no post-Avrami crystallization, the value for this parameter is 0; otherwise, it is different from 0. The Dietz model is actually a modification of a differential form of the Kamal-Chu model.

$$\frac{dX}{dt} = nk(T)(1 - X)t^{n-1} \exp\left[\frac{-aX}{1 - X}\right] \tag{15}$$

We tried to use different value of a to find a good result with experimental values. However, no such a was found. We thus modified the exponent form to $\exp[-aX/1 - aX]$. It can be seen that when increasing a value, the relative crystallinity development becomes slower (Figure 3(e)), which indicates more secondary crystallization. When a equals 0.9, the model can best describe the secondary crystallization (Figure 3(f)).

We should give some comments on these models. First, none of these models can perfectly describe non-isothermal crystallization. The Jeziorny and Kamal-Chu models are not easy to use, since it is difficult to determine crystallization start temperature. It might be better to combine other techniques, like real-time optical microscopy, Raman spectroscopy, and X-ray scattering to get true and reliable crystallization start temperatures. The Ozawa model failed to obtain the crystallization constant and Avrami index. The Nakamura model cannot describe non-isothermal crystallization behavior under high cooling rates. The Dietz model needs to be modified to describe the secondary crystallization process. Second, all these models are tested under quiescent conditions with consideration only to different thermal histories. However, during actual polymer processing, polymer melts are flowing and thus molecules are oriented to a certain degree under certain shear stress. The effect of molecular orientation on crystallization should also be considered. Third, all these models deal with relative crystallinity development. However, it is apparent that different true crystallinity levels will develop under different thermal histories, especially for those polymers with slow crystallization rate. It is more important for us to obtain information on true crystallinity development under different processing conditions. Again, it will be a great advantage to use on-line measurement of molecular orientation and its crystallization during polymer melt flowing to solve the above two problems.

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