

KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION

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ABSTRACT

A kinetic equation of non-isothermal crystallization was derived by extending Avrami's equation to the non-isothermal situation. More crystallization information can be obtained from this kinetic equation. The curves of non-isothermal and isothermal crystallizations were analysed and compared for poly (ethylene terephthalate) (PET), and the results were discussed.

INTRODUCTION

The isothermal crystallization methods generally are used to study the crystallization of polymers since the isothermal kinetics are more classical in theory. But the deficiency of studying the isothermal process of polymers with DSC exist experimentally, i. e., (1) when the rate of crystallization of polymers is very slow, that is, the rate of heat flow is very little, the detection of the change of crystallization with time is difficult; (2) when the rate of crystallization of polymers is very fast, the crystallization process begins to occur before system reaches the desired temperature and it is difficult to define the onset of crystallization. Therefore, if the method of isothermal crystallization is used to determine the crystallization rate of polymers, it is common practice to do isothermal experiments at various temperatures in order to select a suitable range of temperatures. Moreover elaborate procedure is required and little crystallization information can be obtained from the experiment of isothermal crystallization.

If the crystallization process was investigated by means of DSC at the constant heating or cooling rate, not only can the limitations mentioned above be avoided, but the experiment also is easier than isothermal process. In practice, crystallization is seldom encountered under isothermal conditions and usually proceeds under non-isothermal conditions. Especially, such processes take place in the case of the melt-spinning of chemical fibers and the processing of plastics. Therefore, it is necessary to study non-isothermal crystallization processes in a practical sense. Ozawa^[1] was the first to derive a kinetic equation of the non-isothermal process with variable cooling rate, but only Avrami exponent n , which described qualitatively the mechanisms of crystallization, could be obtained from the equation. Jeziorny^[2] utilized isothermal Avrami equation to analyse the curves of the constant cooling rate and to acquire Avrami exponent n and the crystallization rate constant K , and then corrected the rate constant K . This method lacks significance of theory.

In this paper, we have derived a new kinetic equation of non-isothermal

crystallization from which more crystallization information can be acquired when the crystallization is followed by differential scanning calorimetry. The theory and the method obtained have been applied to analyse the crystallization curves of the various cooling rate for poly (ethylene terephthalate).

THEORY

The crystallization kinetics of polymers is normally analysed in terms of the Avrami expression given as follows^[3]

$$1 - Cr = \exp(-Kt^n) \quad (1)$$

where Cr is the relative crystallinity at time t ; K the composite rate constant; and n the Avrami exponent. The numerical value of n is characteristic of certain nucleation and growth mechanisms. From the equation (1), it can be known that a plot of $\ln[-\ln(1 - Cr)]$ versus $\ln t$ yields a straight line; the slope is equal to n and the intercept is equal to $\ln K$. The half life of crystallization (the time required for 50% crystallization) is given by

$$t_{\frac{1}{2}} = (\ln 2 / K)^{1/n} \quad (2)$$

A kinetic equation of crystallization cooled at constant rate was derived by Ozawa^[1] for non-isothermal kinetics of the process of nucleation and its growth.

$$1 - Cr(T) = \exp[-F(T)/R^n] \quad (3)$$

where $Cr(T)$ is the relative crystallinity at temperature T ; R the cooling rate n the Avrami exponent describing the mechanisms of crystallization; and $F(T)$, where is related to the nucleation form, the nucleation rate, and the growth rate of nuclei, is a function of the temperature given as follows:

$$F(T) = g \int_{T_m}^T N_c(\theta) [R_c(T) - R_c(\theta)]^{n-2} V(\theta) d\theta \quad (4)$$

where

$$N_c(\theta) = \int_{T_m}^{\theta} U(T) dT \quad \text{and} \quad R_c(\theta) = \int_{T_m}^{\theta} V(T) dT$$

where $U(T)$ and $V(T)$ are the nucleation rate and the linear growth rate respectively; T_m is the temperature above which the crystallization can not proceed. From equation (3) a plot of $\ln[-\ln(1 - Cr)]$ against $\ln R$ at a given temperature should yield a straight line with a slope of $(-n)$. But more crystallization information can not be obtained from the numerical value of $F(T)$ estimated from the intercept of the line because the content of $F(T)$ is very complicated as given in equation (4).

Now, Avrami equation is extended to non-isothermal situation as follows:

The equation for the rate of the process of crystallization can be expressed by the first order kinetics

$$\frac{dCr}{dt} = SK'(1 - Cr) \quad (5)$$

Where $\frac{dCr}{dt}$ is the rate ; Cr the relative crystallinity ; S the surface area of crystallites and the K' the constant at a given temperature. In order to express the equation (5) using the symbols which have been utilized in the Avrami equation, equation (5) can be written by

$$\frac{dCr}{dt} = (1 - Cr) K (T) n t^{n-1} \quad (6)$$

For the isothermal process, K and n can be considered as a constant respectively. The integration of equation (6) results in equation (1), i. e., Avrami equation.

For the non-isothermal process, Cr is a function of the time or the temperature, and K is not a constant. If the substance is cooled at a rate R , the following expression hold

$$\frac{dT}{dt} = -R \quad (7)$$

and

$$\frac{dCr}{dt} = \frac{dCr}{dT} \cdot \frac{dT}{dt} = -R \frac{dCr}{dT} \quad (8)$$

The integration of equation (7) leads to

$$T = -Rt + T_0 \quad (9)$$

$$\text{then} \quad t = \frac{(T_0 - T)}{R} \quad (10)$$

where T_0 is the temperature at which the crystallization begins to occur. Inserting equations (8) and (10) into (6) yields

$$\frac{dCr(T)}{1 - Cr(T)} = -\frac{n}{R^n} K(T) (T_0 - T)^{n-1} dT \quad (11)$$

Assuming that the value of n remains a constant, the equation above is integrated from T_0 to T , then

$$\ln(1 - Cr(T)) = \frac{n}{R^n} \int_{T_0}^T K(T) (T_0 - T)^{n-1} dT \quad (12)$$

$$\text{or} \quad 1 - Cr(T) = \exp[-F(T)/R^n] \quad (13)$$

$$\text{where} \quad F(T) = -n \int_{T_0}^T K(T) (T_0 - T)^{n-1} dT \quad (14)$$

Equation (12) or (13) and (14) can be used to evaluate crystallization kinetic data at the condition of the various cooling rate. Both n and $F(T)$ can be obtained by plotting $\ln[-\ln(1 - Cr)]$ versus $\ln R$ at a given temperature. $F(T)$ can be obtained as a function of the temperature from the intercepts of the plots at different temperatures. From knowledge of $F(T)$ at various temperatures, the rate constant $K(T)$ can be determined from equation (14), i. e.,

$$K(T) = - \frac{1}{n(T_0 - T)^{n-1}} \cdot \frac{dF(T)}{dT} \quad (15)$$

where T_0 can be obtained as the onset of crystallization shown in Figure 1. Using the values of n and $K(T)$, $t_{\frac{1}{2}}(T)$ can be calculated from equation (2).

For the process of heating at a rate R , the same form as equation (13) can be derived by a similar procedure as mentioned above. $F(T)$ in the equation is slightly different from one obtained in the case of cooling

$$F(T) = n \int_{T_0}^T K(T)(T - T_0)^{n-1} dT \quad (16)$$

EXPERIMENTAL

The sample was poly(ethylene terephthalate) resins and its inherent viscosity was 0.67 determined with an Ubbelohde viscometer in a concentration of 0.5 percent of the sample in o-chlorophenol at 25 °C. Both the isothermal and cooling crystallization were carried out on a differential scanning calorimeter (Perkin-Elmer DSC-2c model). A sample weight of 15 ± 0.1 mg was chosen; a gold pan was used as a reference material; the experiments were carried out under nitrogen atmosphere. The temperature and the energy were calibrated by using metal In. The sample was heated up to 550 K at the rate of 320 K/min, held there for 10 minutes and cooled at the rate of 1.25, 2.5, 5 or 10 K/min respectively. The isotherms were obtained by heating the sample to 550 K at 320 K/min, holding for 10 minutes, and then cooling it to the desired temperature at the rate of 320 K/min.

RESULTS AND DISCUSSION

The cooling crystallization curves of the fraction of uncrystallized material, $1 - Cr(T)$, as a function of temperature, which were obtained by typical DSC thermograms, were shown in Figure 1. According to equation (13), a plot of $\ln[-\ln(1 - Cr)]$ versus $\ln R$ at a given temperature yields a straight line with a slope of $(-n)$ and an intercept of $\ln F(T)$. the results at various temperatures are given in Figure 2. $F(T)$ is the crystallization rate function. The relationship between $\ln F(T)$ and temperature was presented in Figure 3.

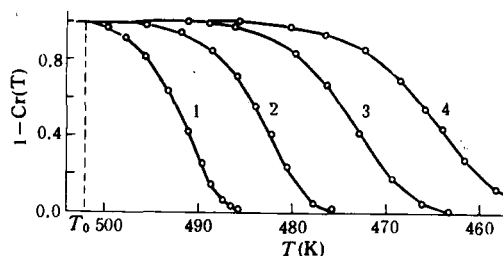


Fig. 1 The cooling crystallization curves of PET at the various cooling rate; 1—1.25K/min, 2—2.5K/min, 3—5K/min, 4—10K/min

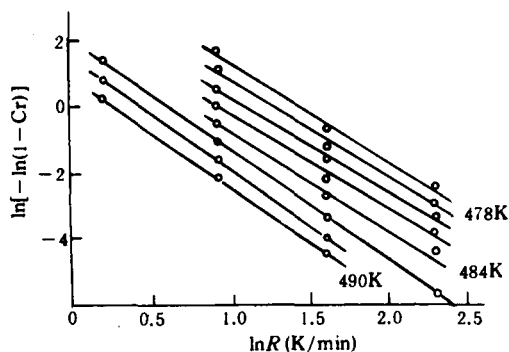


Fig. 2 The plots of $\ln[-\ln(1-Cr)]$ versus $\ln R$ for the dynamic cooling crystallization of poly(ethylene terephthalate)

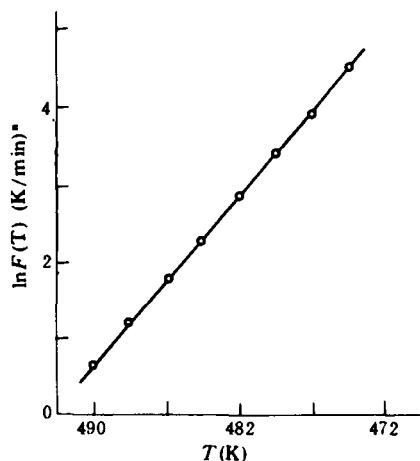


Fig. 3 A plot of logarithmic crystallization rate function vs. temperature

It is obvious that there is a linear correlation between $\ln F(T)$ and T . The linear regression for the curve of $\ln F(T)$ versus T was carried out using the method of least squares and the following equation was given

$$\ln F(T) = -0.2727T + 134.29 \quad (17)$$

The correlation coefficient is equal to 0.99. This indicates that $F(T)$ increases exponentially with dropping temperature in the given range of temperatures. The differentiation of equation (17) results in

$$\frac{dF(T)}{dT} = -0.2727 \exp(-0.2727T + 134.29) \quad (18)$$

From knowledge of n , T and $dF(T)/dT$ values, the crystallization rate constants $K(T)$ at different temperatures can be calculated according to equation (15) and then from values of n and $K(T)$, the crystallization half-period $t_{1/2}$ can be calculated according to equation (2). $K(T)$ and $t_{1/2}(T)$ are the common parameters characterizing the kinetics of crystallization.

To compare with the non-isothermal crystallization, the isothermal crystallizations were carried out at 490, 487.5, 485, 482.5 and 480K respectively. The DSC curves of the isothermal crystallization were analysed according to Avrami equation (1), as shown in Figure 4. The values of n and $t_{1/2}$ obtained from both the isothermal and the non-isothermal crystallization are shown in Figure 5 and Figure 6 respectively.

It can be seen in Figure 5 that the value of n obtained from the cooling

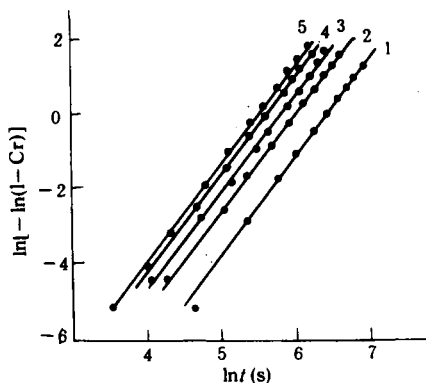


Fig. 4 The analysis of isotherms of the crystallization of poly (ethylene terephthalate) ;
1 — 490K, 2 — 487.5K, 3 — 485K, 4 — 482.5K, 5 — 480K .

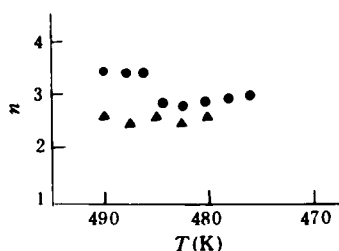


Fig. 5 The relationship between Avrami exponent and crystallization temperature.

● — cooling crystallization, ▲ — isothermal one.

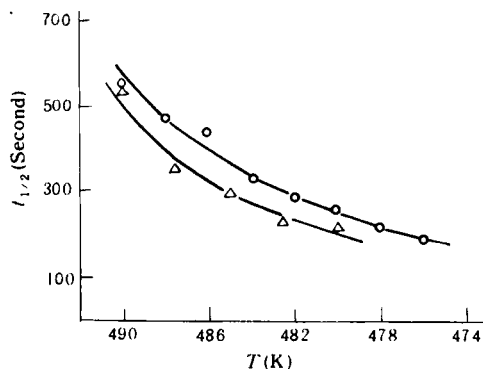


Fig. 6 The relationship between the half life of crystallization and crystallization temperature ;
○ — cooling crystallization, △ — isothermal one.

crystallization curves is slightly larger than that from the isothermal ones. Figure 6 indicates that $t_{1/2}$ of non-isothermal crystallization also is slightly longer than that of isothermal one at a given temperature. The evidence shows that the isothermal crystallization is more rapid than the non-isothermal one. These phenomena may be resulted from that the mechanism of crystallization in the non-isothermal process is different from that in the isothermal one. Ozawa^[1] considered that the discrepancy between the value of n obtained by dynamic observations and those obtained isothermally seem to be caused by the effect of the secondary crystallization. The occurrence of the secondary crystallization can not be verified in our experiments because the secondary crystallization does not appear in the isothermal process in the range of 480—490K, as presented in Figure 4. In addition, there is an interruption of the value of n about 485K. This suggests that the change of the crystallization mechanism occur in the process of cooling. The values of n and $t_{1/2}$ obtained from both the isothermal and the non-isothermal crystallization is slightly different. One of the origins is the distinct mechanisms of crystallization associated with the non-isothermal and the isothermal processes.

This theory is based on the assumption that the value of n is a constant. The

results of the isothermal crystallization at different temperatures show that the value of n almost remains a constant. Although the value of n breaks down in the non-isothermal process, but that the value of n was considered as a constant seems to be a reasonable approximation in the given range of temperatures.

In order to confirm whether the samples with different rate of crystallization can be compared with each other, we select the samples of poly (ethylene terephthalate) with different catalysts and analyse their behavior of cooling and isothermal crystallization respectively. The results show that the parameters of crystallization kinetics obtained from the cooling curves coincide completely with that obtained from the isothermal ones^[4].

When the slow secondary crystallization begins in the process of crystallization, the process does not submit to Avrami equation, i. e., the later stage of crystallization deviates the straight line in the plot of $\ln[-\ln(1-Cr)]$ against $\ln t$. This effect can result in deviation in calculation. Compared to the isothermal crystallization, the effect of secondary process on the cooling crystallization is less because the secondary crystallization can only bring about the deviation of individual points and the effect on the whole result remains less. Ozawa^[1] considered that the secondary crystallization following the primary (Avrami) crystallization is not so serious in cooling observations as in the isothermal ones, since the slow secondary crystallization following the primary one becomes slower at the lower temperature. The secondary crystallization do not appear in the isothermal crystallization in the range of 480—490K, as shown in Figure 4, hence the effects of the secondary crystallization on the results need not be considered.

CONCLUSIONS

The DSC curves of the cooling crystallization at the constant rate were analysed according to the non-isothermal kinetic equation derived in this paper and the parameters characterizing the kinetics of the isothermal crystallization can be obtained from the equation in the range of given temperatures. The value of n derived from the non-isothermal kinetics is slightly larger than that from the isothermal ones and $K(T)$ is slightly smaller than that from the isothermal ones. The crystallization kinetic parameters of the samples with different rates of crystallization can be compared with each other. The method of the non-isothermal crystallization is easier than the isothermal one in experiment and more information of crystallization can be obtained by using the non-isothermal kinetic equation developed in this paper. The agreement between the results of the isothermal and cooling crystallization is satisfactory.

Keywords :

Non-isothermal crystallization, Crystallization Kinetics, Poly (ethylene terephthalate), Differential scanning calorimeter (DSC).

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