Crystallization Behavior of Polytetrafluoroethylene (PTFE)

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ABSTRACT: For some polymers such as PTFE, the crystallization is so rapid that it is difficult to observe isothermal crystallization by differential scanning calorimetry (DSC). In this investigation, first, isothermal crystallization kinetics of PTFE was followed by DSC and the results were analyzed by the Avrami method, which showed that PTFE crystallizes one-dimensionally from preexisting nuclei, presumably impurities. Furthermore, the crystallization activation energy, the equilibrium melting point, and the nucleation rate parameter K_g were calculated in the isothermal crystallization. Second, nonisothermal crystallization was also studied and the result was in accordance with the results of isothermal crystallization. Then, the Kissinger method was used to investigate the activation energy of PTFE in the nonisothermal crystallization. Third, the effect of glass fiber (used as filling) was investigated on crystallization of PTFE matrix. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 990–996, 2002

Key words: PTFE; glass fiber; composites; isothermal; nonisothermal; crystallization; kinetics; differential scanning calorimetry

INTRODUCTION

Plastics, especially compositionally identical plastics (matrix) products may exhibit different properties such as toughness, elasticity, transparency, or permeability. These properties are dependent on the micromorphology of the material, which in turn is determined by the raw and processed materials and the thermomechanical history that the material experiences during processing. In partially crystalline polymers (matrix) like PTFE, solidification during processing is accompanied by crystallization, either under isothermal or nonisothermal conditions. The resulting microstructure, as reflected by structure and orientation, has a significant effect on the ultimate properties of the product. Thus the study on crystallization of polymers is necessary to understand the microstructure of polymer products.

The crystallization of PTFE is so rapid that it is difficult to observe isothermal crystallization thermograms by differential scanning calorimetry (DSC). So far, no study on isothermal crystallization of PTFE has yet been reported. However, a study on nonisothermal crystallization of PTFE was previously reported.[1]

In this investigation isothermal and nonisothermal crystallization were followed by DSC, respectively. A similar result, that PTFE crystallizes one-dimensionally, was obtained, from the data of isothermal and nonisothermal crystallization, respectively. This result was in accordance with the microstructure of various observed PTFE crystals.[2–5] The activation energy of crystallization was characterized by different methods.

EXPERIMENTAL

Preparation and properties of pure PTFE and PTFE composite samples was previously discussed in detail by Wang and coworkers.[6]
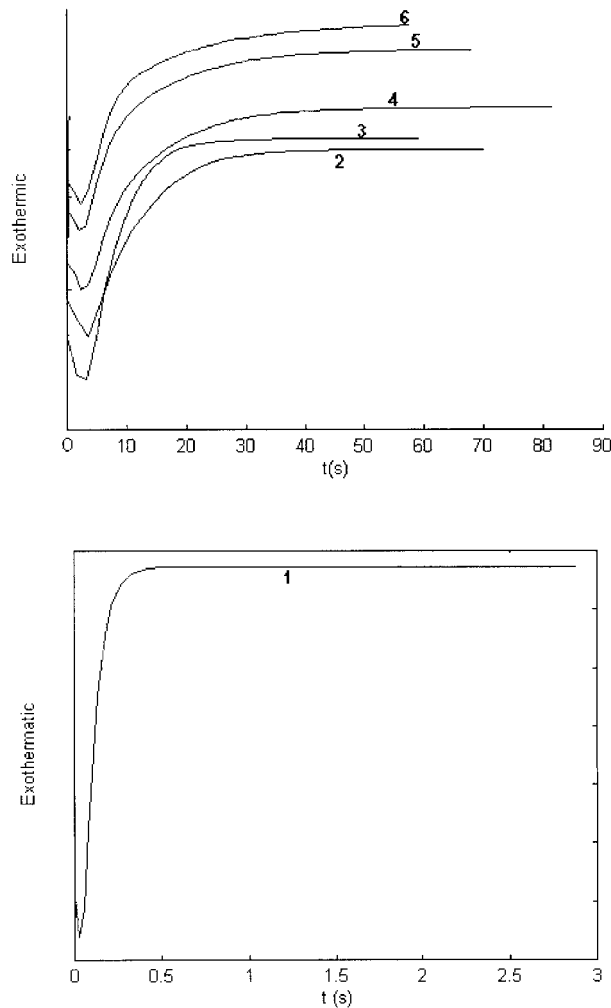
Figure 1 DSC thermograms of isothermal crystallization at different T_c: (1) 569 K; (2) 577 K; (3) 585 K; (4) 586 K; (5) 587 K; (6) 588 K.

The kinetics of the isothermal and nonisothermal crystallization process were followed using a Perkin–Elmer DSC-7 analyzer (Perkin Elmer Cetus, Norwalk, CT). The experiments were carried out under nitrogen, and the calibration was performed with indium and zinc.

For isothermal crystallization, samples were heated to 653 K (heating rate is 20 K/min, beginning to melt while heated to 600 K) and were held at the molten state for 3 min to erase the former thermal history, after which they were rapidly cooled at the maximum cooling rate (200 K/min) to the crystallization temperatures T_c (588, 587, 586, 585, 577, and 569 K). T_c was then held constant until crystallization was completed.

For nonisothermal crystallization, the melt was cooled at different rates (1.3, 2.5, 5, 10, 20, 40, and 60 K/min). The cooling rate was held constant

until the temperature of the samples was under 473 K.

RESULTS AND DISCUSSION

Isothermal Crystallization of PTFE

The isothermal crystallization was followed by DSC, and DSC thermograms (Fig. 1) were obtained at definite temperatures. Because the degree of regularity of the PTFE structure is higher than that of most other polymers, PTFE can crystallize more easily and faster than the others. During the period when the melt was cooled to the definite temperatures, PTFE had begun to crystallize; thus DSC thermograms of isothermal crystallization were not integral (Fig. 1). The relative amount of crystallinity, which developed at a definite temperature, increased with increasing crystallization time (Fig. 2).

The Avrami equation,[7] shown as follows, was used to analyze the DSC data in Figure 1:

$$X_t = \frac{X_{c(t)}}{X_{c(\infty)}} = \frac{\displaystyle\int_0^t (dH_c/dt)\,dt}{\displaystyle\int_0^\infty (dH_c/dt)\,dt} = 1 - \exp(-kt^n) \quad (1)$$

where $X_{c(t)}$ and $X_{c(\infty)}$ are the degree of crystallinity at time t and at the end of crystallization, respec-
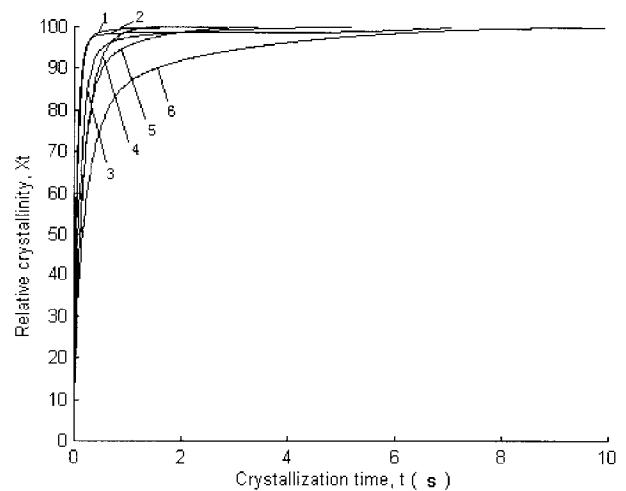
Figure 2 Development of relative crystallization with time for isothermal crystallization of PTFE at the indicated temperatures: (1) 569 K; (2) 577 K; (3) 585 K; (4) 586 K; (5) 587 K; (6) 588 K.
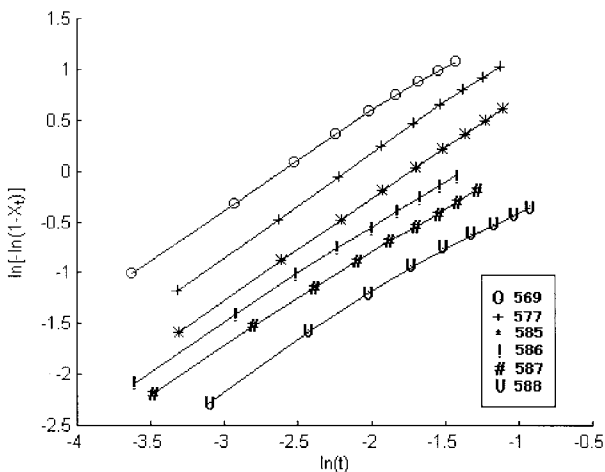
Figure 3 Plot of $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$ (in min) for isothermal crystallization of PTFE at the indicated temperatures.

tively; dH_c/dt is the rate of crystallization heat evolution at time t; k is a rate constant; and n is the Avrami exponent, an integer between 1 and 4, depending on the geometry of the growing entities and the nature of the primary nucleation.
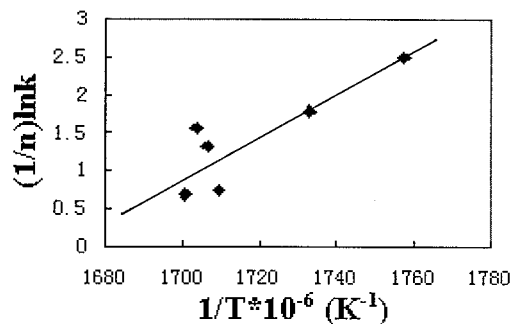
Although the data in Figure 1 were not integral, the remnant data in Figure 1 were still analyzed by the Avrami equation and satisfying Avrami curves were obtained (Fig. 3). The Avrami parameters n and k could be estimated (Table I) from the slopes and the intercepts, respectively, in the plots of $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$, as shown in Figure 3. From Table I, it was obvious that the average value of the Avrami exponent is near 1. It could be concluded from the fact that the crystals of PTFE grow one-dimensionally from the preexisting nuclei. In addition, the values of the crystallization rate parameters k are apt to decrease with increasing crystallization temperature because of a gradual decrease in the degree of supercooling.
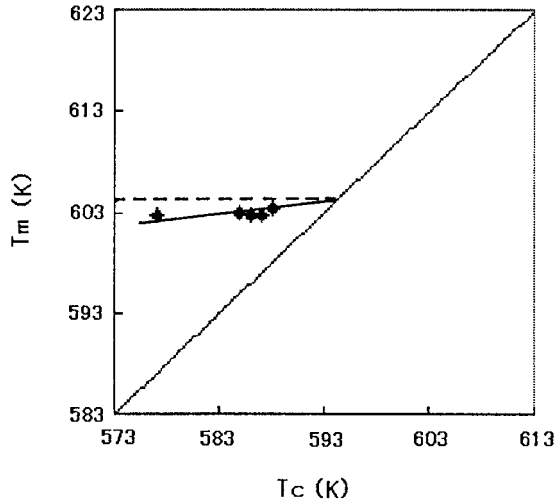

Figure 4 Plot of $(1/n)\ln k$ versus $1/T$ for the isothermal crystallization of PTFE.

The crystallization rate parameter K can also be approximately described as follows[9]:

$$\frac{1}{n} \ln K = \ln k_0 - \frac{\Delta E}{RT} \tag{2}$$

where k_0 is a temperature-independent preexponential factor; ΔE is a total activation energy, which consists of the transport activation energy ΔE^* and the nucleation activation energy ΔF (ΔE^* refers to the activation energy required to transport molecular segments across the phase boundary to the crystallization surface and ΔF is the free energy of formation of the critical size crystal nuclei at crystallization temperature T_c); R is the universal gas constant; and T is the absolute temperature. The slopes of the Arrhenius plots (Fig. 4) of $(1/n)\ln k$ against $1/T$ determined $\Delta E/R$, and ΔE was estimated to be -330 kJ/mL. The negative sign showed that it had to release energy while transforming the molten fluid into the crystalline state.

According to theoretical considerations by Hoffman and Weeks,[10] the equilibrium melting point of polymers may be deduced solely from DSC measurements:

Table I Isothermal Crystallization Data for PTFE

T_c (K)	$\Delta H_m{}^a$ (J/g)	$X_c{}^b$ (%)	N	K (s^{-1})	t'_{max} (s)	T_{max} (s)	$t_{1/2}$ (s)	$\tau_{1/2}$ (s^{-1})
569	47.405	53.26	0.96	12.12	0.029	—	0.057	17.54
577	46.038	51.73	1.01	5.97	0.042	0.0018	0.116	8.62
585	47.851	53.77	1.006	2.09	0.056	0.0029	0.332	3.01
586	46.308	52.03	0.94	3.73	0.046	—	0.167	5.99
587	43.367	48.73	0.91	4.74	0.038	—	0.121	8.26
588	46.972	52.78	0.87	1.97	0.040	—	0.301	3.32

 a ΔH_m; PTFE; T_c.
 b The same as in Table II.

Figure 5 Application of Hoffman–Weeks approach to PTFE for determining its equilibrium melting temperature T_m°.

$$T_m = T_m^\circ \left(1 - \frac{1}{2\phi}\right) + \frac{1}{2\phi}T_c \quad (3)$$

where T_m° is the equilibrium melting point and ϕ is the lamellar thickening factor, which describes the growth of lamellar thickness during crystallization. Under equilibrium conditions, $\phi = 1$. At the higher crystallization temperatures, the slope of the plots was 0.5 and extrapolated to a thermodynamic melting point of T_m°.

From the Hoffman–Weeks method , the equilibrium melting point of PTFE was determined to be 604 K for PTFE (Fig. 5).

From the heating DSC curve of PTFE,[8] T_g was determined to be 184.6°C. The crystal growth rate G was analyzed by means of the Lauritzen–Hoffman[11] theory developed for homopolymers. According to this theory, G is described by the following:

$$\ln G + \frac{U^*}{2.3R(T_c - T_\infty)} = \ln G_0 - \frac{K_g}{2.3T_c(\Delta T)f} \quad (4)$$

where G_0 is a preexponential factor containing quantities that do not have a strong dependence on temperature; U^* is the activation energy that governs the short distance diffusion (or transport) of the crystallizable segments from the melt across the phase boundary to the site of crystallization; T_∞ is a hypothetical temperature below which all molecular motion associated with the viscous flow ceases and it is related to T_g. We can employ the standard values,[12,13] $U^* = 1500$ cal/

mol, $T_\infty = T_g - 30$. R is the university gas constant, the value of which is 8.31 J mol^{-1} K^{-1}; T_c is the crystallization temperature; K_g is a nucleation constant; ΔT is the degree of supercooling ($\Delta T = T_m^\circ - T_c$, where T_m° is the equilibrium melting temperature); and f is a correction factor to account for the variation ΔH_f (the bulk enthalpy of fusion per unit volume for fully crystalline polymer) with temperature, $f = 2T_c/T_m^\circ + T_c$. Growth rates at relatively low degrees of supercooling (the only ones accessible here) are well known to exert a relatively negligible effect on rearranging eq. (4). Plots of the left-hand side of eq. (4) against $1/[T_c(\Delta T)f]$ should yield a straight line with $\ln G_0$ as intercept and $(-K_g/2.3)$ as slope. Thus from Figure 6, K_g was 1.545×10^4 K^2 and G_0 was 84.39.

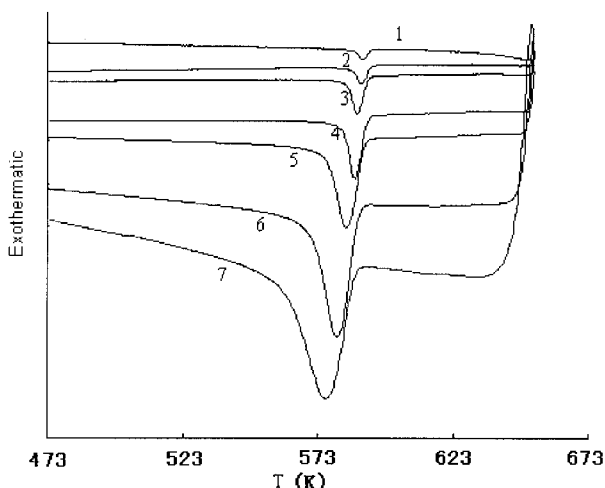## Nonisothermal Crystallization of PTFE

The crystallization exotherms of PTFE at different cooling rates are illustrated in Figure 7. As can be seen, the peak temperature for maximum crystallization to occur (T_p) shifted to a low-temperature region with increasing cooling rate β. Data of nonisothermal crystallization are listed in Table II.

Figures 8 and 9 show the developments of relative degree of crystallinity with temperature and time, respectively. As can be seen, when the cooling rate was above 10 K/min, the effect of the cooling rate on relative degree of crystallinity was less than that when the cooling rate was below 10 K/min.

According to the Ozawa equation,[14] when polymer crystallizes from preexisting nuclei, the Avrami exponent n can be expressed in the following form:
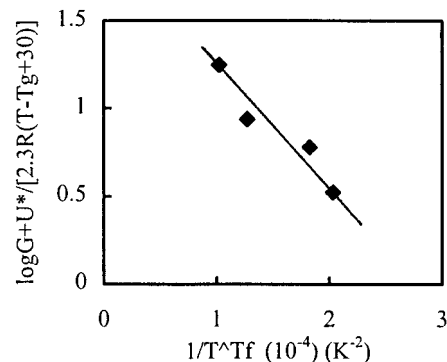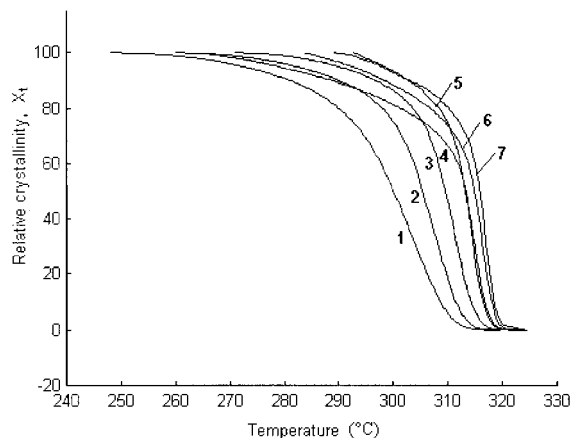

Figure 6 Growth rate data for isothermal melt crystallization of PTFE.

Figure 7 Heat flow curves versus temperature during the nonisothermal crystallization of PTFE at the indicated cooling rates: (1) 1.3 K/min; (2) 2.5 K/min; (3) 5 K/min; (4) 10 K/min; (5) 20 K/min; (6) 40 K/min; (7) 60 K/min.

Figure 8 Relative degree of crystallinity versus temperature during nonisothermal crystallization at the indicated rates for PTFE: (1) 1.3 K/min; (2) 2.5 K/min; (3) 5 K/min; (4) 10 K/min; (5) 20 K/min; (6) 40 K/min; (7) 60 K/min.

$$\ln[-\ln(1 - X_t)] = \ln[\chi(T)] - n \ln(\beta) \qquad (5)$$

where $\chi(T)$ is the cooling function and β is the cooling rate. The results of the Ozawa analysis are shown in Figure 10, plotted as $\ln[-\ln(1 - X_t)]$ versus $\ln \beta$, for temperatures in the range from 595 to 571 K. The Ozawa plot resulted in a series of parallel lines of slope near 1. It could be included that PTFE crystallizes one-dimensionally at a constant cooling rate. This result was in accordance with the one-dimensional growth mechanism obtained by isothermal crystallization of PTFE. It was also in accordance with the result of Ozawa on nonisothermal crystallization of a few PTFE products,[1] and was in accordance with the microstructure of various observed PTFE crystals.[2–5]

Figure 11 shows plots of $\ln[-\ln(1 - X_t)] + \ln \beta$ versus temperature T. As can clearly be seen, when the temperature was above 583 K, the value of $\ln[-\ln(1 - X_t)] + \ln \beta$ rapidly increased with a reduction of temperature. However, when the temperature was below 583 K, the value of $\ln[-\ln(1 - X_t)] + \ln \beta$ increased slowly and even remained constant when the temperature was below 563 K. Thus, according to Figure 11, the relationship between X_t and β could be easily obtained at a considered temperature.

Considering the variation of the peak temperature T_p with the cooling rate β in differential thermal analysis, the activation energy ΔE could be determined by the Kissinger equation in the following form[15]:

Table II Data of Nonisothermal Crystallization for PTFE

Number	Cooling Rate (K/min)	T_p (K)	T_{max} (min)	$-\Delta H_c$ (J/g)	X_t^a (%)	X_c^b (%)
1	1.3	589.66	7.1	29.64	25.56	33.30
2	2.5	589.05	3.07	35.57	37.42	39.97
3	5	587.50	2.4	35.57	38.55	39.97
4	10	586.70	1.4	30.72	41.24	34.52
5	20	583.57	0.85	30.36	41.86	34.11
6	40	580.24	0.31	31.32	37.41	35.19
7	60	575.91	0.26	29.31	36.77	32.93

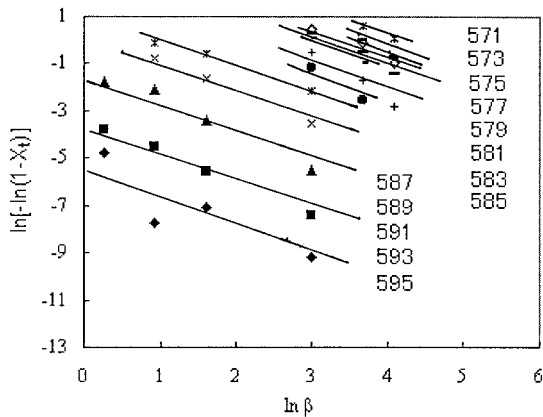[a] X_t, relative degree of crystallinity at the peak enthalpy.
[b] X_c, degree of crystallinity determined as $X_c = \Delta H_c / \Delta H_U \times 100\%$. $\Delta H_U = 69$ J/g.[8]
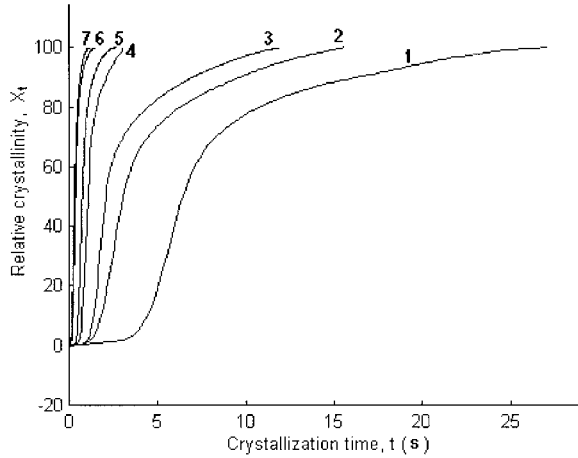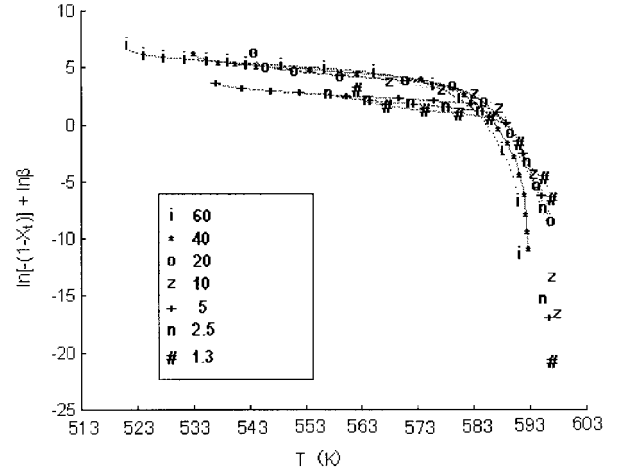
Figure 9 Development of relative degree of crystallinity with time for nonisothermal crystallization of PTFE: (1) 1.3 K/min; (2) 2.5 K/min; (3) 5 K/min; (4) 10 K/min; (5) 20 K/min; (6) 40 K/min; (7) 60 K/min.

Figure 11 Plots of $\{\ln[-\ln(1 - X_t)] + \ln(\beta)\}$ versus T from nonisothermal crystallization data of PTFE.

$$\frac{d\left(\ln\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{\Delta E}{R} \tag{6}$$

where the parameters are as previously defined. According to the data shown in Table II and eq. (6), the Kissinger plot was obtained to determine the activation energy of nonisothermal crystallization (Fig. 12). However, from Figure 12 we see that the Kissinger plot is not a straight line. When the cooling rate was 20, 40, or 60 K/min, the value of the slope was lower than the corresponding value of the line obtained by the experimental data at cooling rates of 1.3, 2.5, 5, and 10 K/min.

It did not seem to fit the Kissinger equation. One of the reasons may be that some assumptions were used to obtain the Kissinger equation. Through further consideration, however, both activation energies 1846 and 478 kJ/mL were obtained by the slopes of the two straight lines, 222.17 and 7.55, respectively. When the cooling rate was higher, the activation energy was lower, which seemed reasonable.

Effect of Glass Fiber on Crystallization of PTFE

According to the Dobreva method,[16] the cooling rate β and the undercooling ΔT_p are related as follows:

$$\log \beta = C - \frac{B}{2.3\Delta T_p^2} \tag{7}$$

Figure 10 Ozawa plots of $\ln[-\ln(1 - X_t)]$ against $\ln(\beta_i)$ from the data of nonisothermal crystallization of PTFE.
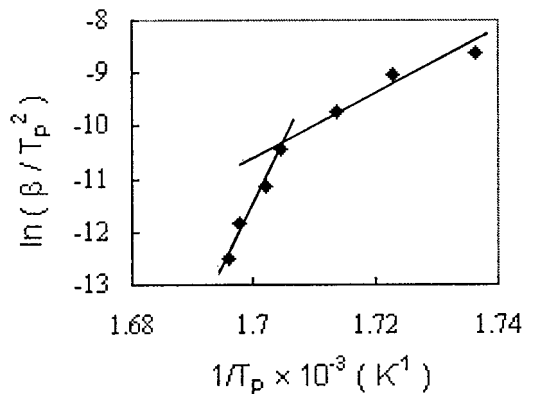

Figure 12 Kissinger plots for determining nonisothermal crystallization activation energy.
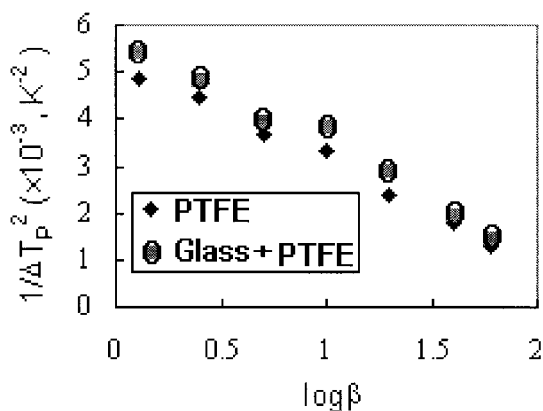
Figure 13 Rate dependence of the crystallization temperature in coordinates $1/\Delta T_p^2$ versus $\log \beta$ according to eq. (7).

The nucleation activity of fillers ϕ can be determined by the ratio:

$$\phi = \frac{B^*}{B} \tag{8}$$

where B and B^* are the slopes of the $\log \beta$ versus $1/T_p^2$ dependence for both the homogeneous case and the heterogeneous case, respectively; C is constant; $\Delta T_p = T_m - T_p$, whereas T_p denotes the temperature corresponding to the peak of the crystallization curve.

Figure 13 is plotted in terms of the nonisothermal crystallization data of pure PTFE and PTFE filled with glass fiber. It was calculated by virtue of eq. (7) that $\phi = 0.97 \approx 1$, which means that glass fiber acts as a poor nucleation agent.

Further experiments showed that the influence of the glass fiber on the degree of crystallinity X_c was also negligible. The heat of crystallization of PTFE filled with glass fiber was the same as the heat of crystallization of pure PTFE resin.

CONCLUSIONS

This work has demonstrated that the crystallization kinetics of PTFE, both in isothermal and dynamical processes, can be studied effectively by DSC technology. The data of isothermal and nonisothermal crystallization, obtained by DSC, were analyzed by the Avrami equation and the Ozawa method, respectively. Similar results confirmed that PTFE crystals grow one-dimensionally. Glass fibers could not obviously affect the crystallization of the PTFE matrix. From the data of isothermal crystallization, according to Arrhenius form, the activation energy was estimated to be -330 kJ/mL; by the Hoffman–Weeks method the equilibrium melting point of PTFE was determined to be 604 K; the nucleation constant K_g was 1.545×10^4 K^2; and the preexponential factor G_0 was 84.39. According to the Kissinger equation, the activation energies of nonisothermal crystallization for PTFE are about 1846 and 478 kJ/mL. In different ranges of cooling rates, the difference of the activation energies was acceptable for the actual crystallization process, and this may be helpful both to understand and to control the actual crystallization process.

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