

Crystallization Kinetics of Toughed Poly(butylene terephthalate)/Polycarbonate Blends

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ABSTRACT: The crystallization kinetics of pure poly(butylene terephthalate) (PBT) and toughed modification PBT/polycarbonate (PC) blends with ethylene-butylacrylate-glycidyl methacrylate copolymer (PTW) and ethylene-1-octylene copolymer (POE) were studied. For nonisothermal crystallization process studies, the Ozawa theory and an equation combining the Avrami and Ozawa equation are used. It is found that the Ozawa analysis fails to provide an adequate description of the nonisothermal crystallization process in PBT, PBT/PC, and toughed PBT/PC blends, while the combination of the Avrami and Ozawa equations exhibit great advantages in treating the nonisothermal crystallization kinetics. The activation energies are determined by the Kissinger method for nonisothermal crystallization. The activation energy for PBT/PC/PTW/POE blend is

greater than those of PBT/PC, and PBT/PC/POE blends. Isothermal crystallization processes were studied by the Avrami equation. The results show that the values of the Avrami exponent n for PBT, PBT/PC, and toughed PBT/PC blends are 3.8, 3.0, and 2.8–3.2, respectively. The Avrami rate constant K for PBT, PBT/PC, and toughed PBT/PC blends increase in following order: $K_{\text{PBT/PC}} < K_{\text{PBT/PC/POE}} < K_{\text{PBT/PC/PTW/POE}} < K_{\text{PBT}}$ © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1295–1308, 2006

Key words: poly(butylene terephthalate); polycarbonate; ethylene-butylacrylate-glycidyl methacrylate copolymer; ethylene-1-octylene copolymer; crystallization kinetics; nonisothermal; isothermal

INTRODUCTION

Polymer alloys are important engineering materials whose ultimate properties may be tailored by taking advantage of the properties of constituent polymers. In binary poly(butylene terephthalate) (PBT)/polycarbonate (PC) blends, PBT imparts solvent resistance to the blends, while PC may increase the use temperature. PBT is known to crystallize rapidly but is somewhat brittle in spite of its low glass-transition temperature. PC does not normally crystallize and has a much higher glass-transition temperature. However, commercial PBT/PC blends are found to undergo severe brittleness and require the addition of impact modifiers to enhance its performance under impact resistance tests, mainly for notched test specimens. Some impact modifiers have been added into PBT/PC blends to improve its toughness.¹ Ethylene-1-octylene copolymer (POE) is a polyolefin elastomer with a narrow molecular weight distribution and homogeneous octene distribution, and exhibits the advantage of thermoplastic processability; its elastomeric nature has allowed it to be used as an impact modifier for

PBT² and PP.³ Ethylene-glycidyl methacrylate copolymer (EGMA) has epoxy groups (glycidyl) and can react with carboxyl (preferentially) or hydroxyl functional groups. Because of its elastomeric nature and reactivity, EGMA has been used as an impact modifier for engineering thermoplastics and thermoplastic/polyolefin blends, such as poly(ethylene terephthalate) (PET),⁴ PBT,⁵ PBT/polypropylene (PP),⁶ and PBT/POE.⁷

It is well known that the physical and mechanical properties of semicrystalline polymers depend to a great extent on the degree of crystallization, which is in turn affected by the crystallization conditions. The crystal structure and morphology are established during the solidification process that takes place through the nucleation and spherulite development. In practical processing, such as extrusion, molding, and foam forming, crystallization usually proceeds under isothermal and nonisothermal conditions. Therefore, the investigation of the kinetics of crystallization has a considerable practical significance. Moreover, kinetic crystallization treatments can be used to elucidate the mechanism of nucleation and growth in polymeric crystals, which is without doubt of great theoretical interest.

Isothermal crystallization measurements are usually used to study the crystallization behavior of polymers, since their theoretical analysis is relatively easy. The

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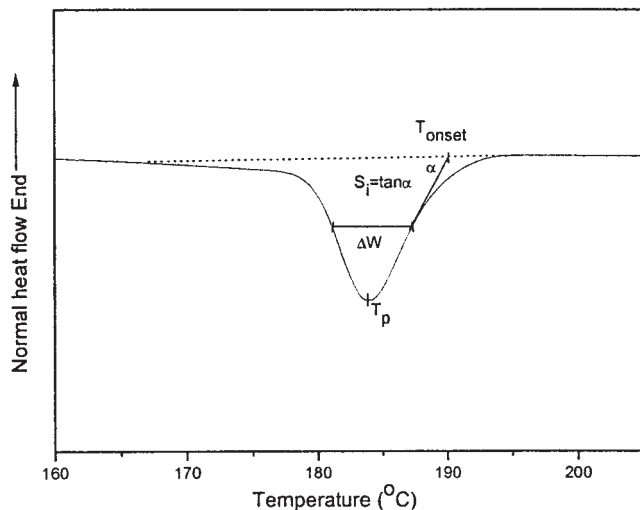


Figure 1 Schematic representation of all the parameters of crystallization during the nonthermal crystallization process.

treatment of nonisothermal crystallization data, in which the samples are observed at a constant cooling rate, is theoretically more complicated,⁸ although very important, since this type of crystallization approaches more closely the industrial conditions of polymer processing such as extrusion molding, and melt-spinning of synthetic fibers.

To control the rate of crystallization and the degree of crystallinity and obtain materials with better physical properties, a great deal of effort has been devoted into studying the crystallization kinetics and determining the change in material properties.^{9,10} The melting and crystallization behavior of neat PBT^{11–16} and the related binary blend of PBT/PC^{17–22} have been reported. A few studies observed the depression of crystallization kinetics of PBT in the presence of PC.^{20–22} Unfortunately, there is little information in the literature about the melting and crystallization behavior of PBT in the toughed PBT/PC blends.

Poly(ethylene-butylacrylate-glycidyl methacrylate) (PTW) is a copolymer with epoxy groups (glycidyl) that can react with carboxyl (preferentially) or hydroxyl functional groups, and with butylacrylate segment that provides very good low temperature properties. Therefore, PTW appears to be an attractive impact modifier because of both reactive processing and rubbery toughening.

To improve the toughness of PBT/PC blend, PTW and POE were used as modifiers in this study. The purpose of this report was to investigate the isothermal and nonisothermal crystallization kinetics of the PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends by using differential scanning calorimetry (DSC).

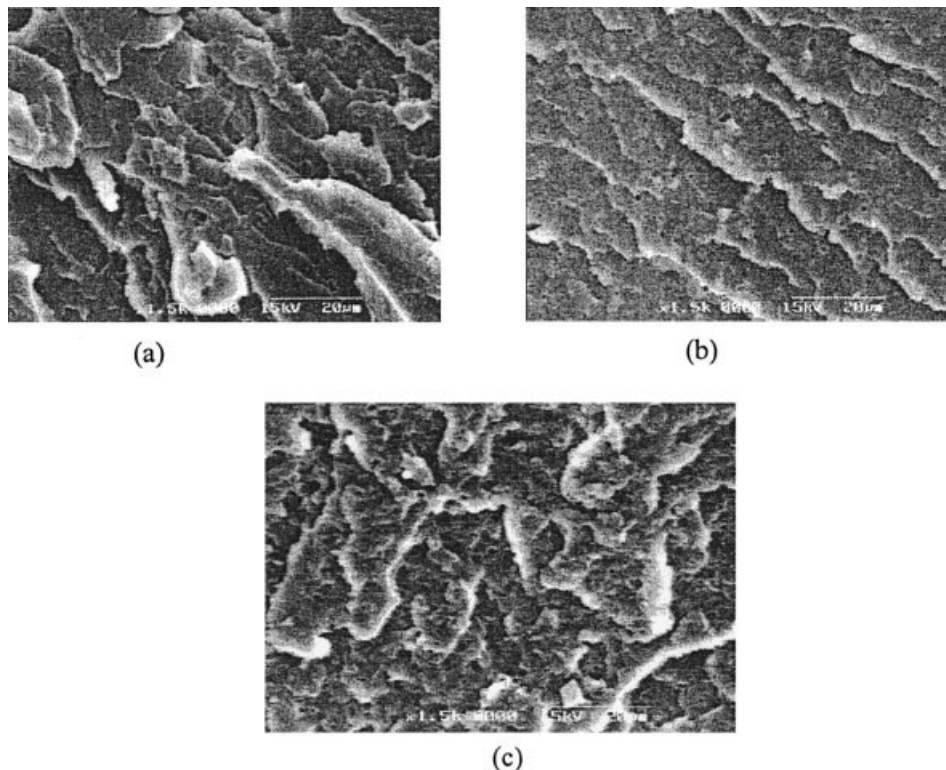


Figure 2 The morphology of PBT/PC 50/50 (a), PBT/PC/POE 50/50/3.5 (b), and PBT/PC/PTW/POE 50/50/3.5/3.5 (c) blends.

EXPERIMENTAL

Materials and preparation

PBT was L2100G (Yizheng Chemical Fiber Group, China). PC was PC110 (Chimei-Asahi, Taiwan, China). PTW was Elvaloy PTW (Du Pont, USA). POE was Engage 8180 (Du Pont-Dow, USA).

PBT and PC particulates were dried at 120°C for 4 h in a vacuum oven before processing. The blends comprised 50 phr PBT and 50 phr PC by weight.

The blends were extruded using a Berstoff twin-screw extruder (type ZE25, L/D ratio, 41; screw diameter, 25 mm; Germany) at a screw speed of 300 rpm and torques of 50–70%. The temperature profiles of the barrel were 40–230–230–235–235–240–240–245–250°C from the hopper to the die. The extruded blends were dried in an air oven for 4 h at 100°C. Injection molding was carried out in a plastic injection molding machine (HTB110X/1, China), the barrel temperature profiles for injection molding were 240–250–250–250–259°C, and the mold temperature was at 50°C.

Differential scanning calorimetry

A DSC (Perkin-Elmer DSC-1, USA) was used to analyze the isothermal and subsequent melting behavior and nonisothermal crystallization. To be compared with the PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends, PBT was extruded under identical processing conditions to those of blends. Samples weighing 6–8 mg for DSC analysis were cut from the injection molded bars. It is worth noting that each sample was used only once and all the runs were carried out under nitrogen atmosphere to prevent extensive thermal degradation.

The isothermal crystallization and melting process of PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends were performed as follows: the samples were heated at 20°C/min from 20°C to 250°C and kept for 3 min to eliminate any previous thermal history; then they were cooled at 150°C/min to the predetermined crystallization temperature (T_c), and maintained at T_c for 15 min, necessary for DSC trace return to the calorimeter baseline. The cooled sample was then reheated at a rate of 20°C/min to 250°C. The exothermal curves of heat flow as a function of time were recorded to analyze the melting behaviors. The melting temperature (T_m) and enthalpy of fusion (ΔH_m) values of the composites were calculated from the maximum and the area under the endothermic peak, respectively.

The nonisothermal crystallization process of PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends were performed as follows: the samples were heated at 20°C/min from 20°C to 250°C and kept for 3 min to eliminate the thermal history before cooling at a specified cooling rate. The samples were then cooled

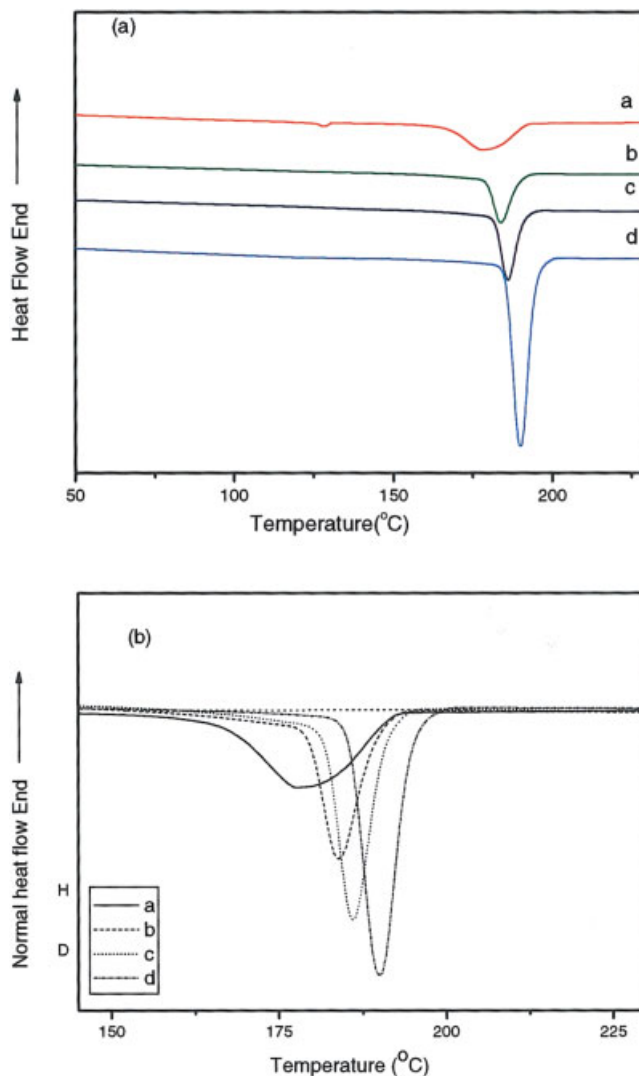


Figure 3 (a) DSC thermograms (b) normalized DSC thermograms during the nonthermal crystallization process at a cooling rate of 10°C/min for PBT (d) and PBT/PC (a), PBT/PC/POE (b), and PBT/PC/PTW/POE (c) blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to 20°C at constant cooling rate of 2.5, 5, 10, 20°C/min. The exothermal curves were recorded.

Nonisothermal crystallization parameters

From the DSC curves of samples crystallized from the melt state at a given cooling rate, some useful parameters can be obtained to describe the nonisothermal crystallization.^{23–25}

These parameters are defined next and are illustrated in Figure 1.

1. The peak temperature of crystallization (T_p) is the temperature at which the value of the heat flow is maximum.

TABLE I
Various Parameters of PBT and PBT/PC, PBT/PC/POE,
and PBT/PC/PTW/POE Blends Obtained from the
Nonisothermal Crystallization Exotherm at a Cooling
Rate of 10°C/mm

Samples	T_p (°C)	T_{onset} (°C)	$T_{\text{onset}} - T_p$ (°C)	S_i	ΔW
PBT	190.0	196.5	6.5	1.36	5.9
PBT/PC	177.1	191.8	14.7	0.147	15.7
PBT/PC/POE	178.0	190.6	12.6	0.727	6.3
PBT/PC/PTW/POE	185.8	192.0	6.2	1.134	5.7

2. The quantity $T_{\text{onset}} - T_p$, where T_{onset} is the temperature at the intercept of the tangents at the baseline and the high-temperature side of the exotherm.

3. The initial slope of the exotherm (S_i) is the slope at inflection on the high-temperature side of the exotherm.
4. The width at half-height of the exotherm peak (ΔW) determined after normalization of the peak to a constant mass of the samples.

The parameter S_i has been measured as the rate of nucleation. The parameter $T_{\text{onset}} - T_p$ is a measure of the overall rate of crystallization. The smaller $T_{\text{onset}} - T_p$ is, the greater the crystallization rate is, ΔW is a measure of the crystallite size distribution. The smaller ΔW is, the narrower the crystallite size distribution is.

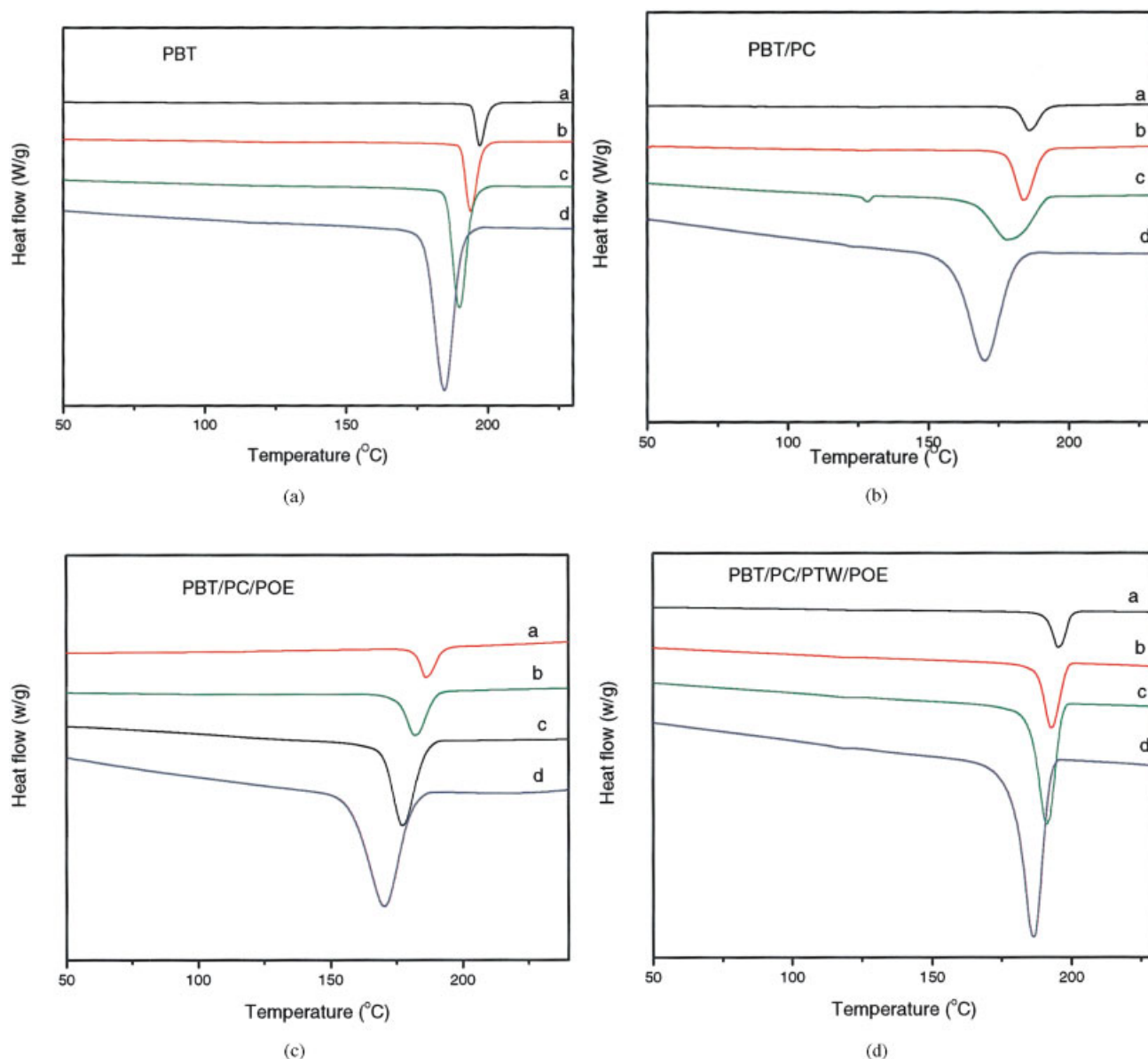


Figure 4 Heat flow as a function of temperature during nonisothermal crystallization at different cooling rates by DSC for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends (a) 2.5°C/min (b) 5°C/min (c) 10°C/min (d) 20°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

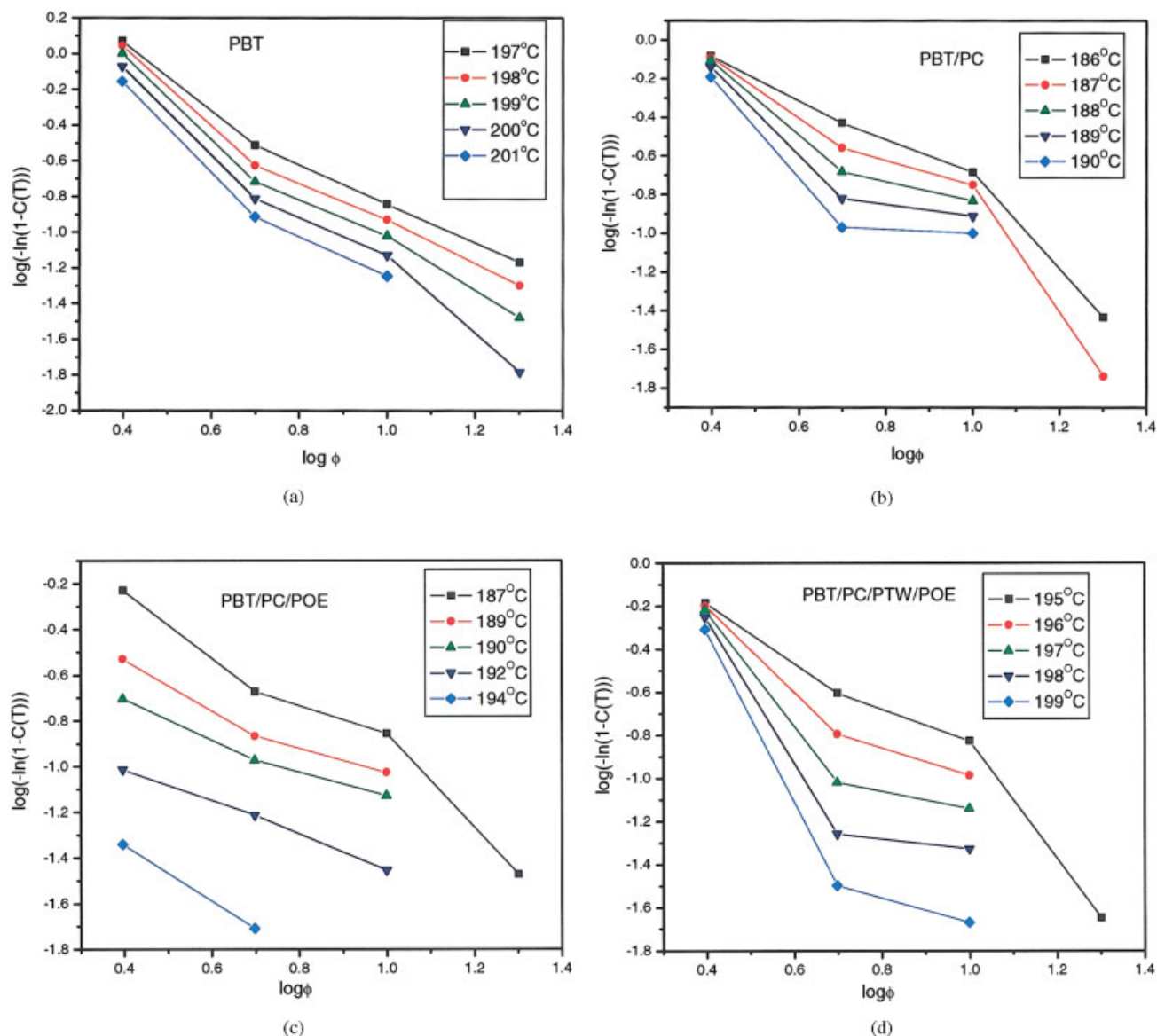


Figure 5 Ozawa plots of $\log[-\ln(1-C(T))]$ versus $\log \Phi$ at the indicated temperature for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scanning electron microscopy (sem) analysis

A SEM (Hitachi S-2150) was used to examine the morphology of the blends. The samples were fractured in liquid nitrogen and covered with a thin layer of gold for further observation.

RESULTS AND DISCUSSION

Morphology

Figure 2 shows the SEM fractographs of PBT/PC (50/50), PBT/PC/POE (50/50/3.5), PBT/PC/PTW/POE (50/50/3.5/3.5) blends. As can be seen from the Figure, the POE particles were dispersed as very large sizes in the PBT/PC/POE blends. However, in the

PBT/PC/PTW/POE blend, the POE particles were dispersed in small sizes because of the presence of PTW that acts as a compatibilizer for promoting a fine dispersion of the POE particles.

Nonisothermal crystallization analysis

Nonisothermal crystallization kinetics of polymers is of importance in process modeling and crystallization control.^{26,27} Recently, the kinetic parameters derived from isothermal experiments were also used to predict the nonisothermal crystallization behavior.

Figure 3(a) shows the DSC cooling thermograms of PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends, and the normalized DSC cooling thermo-

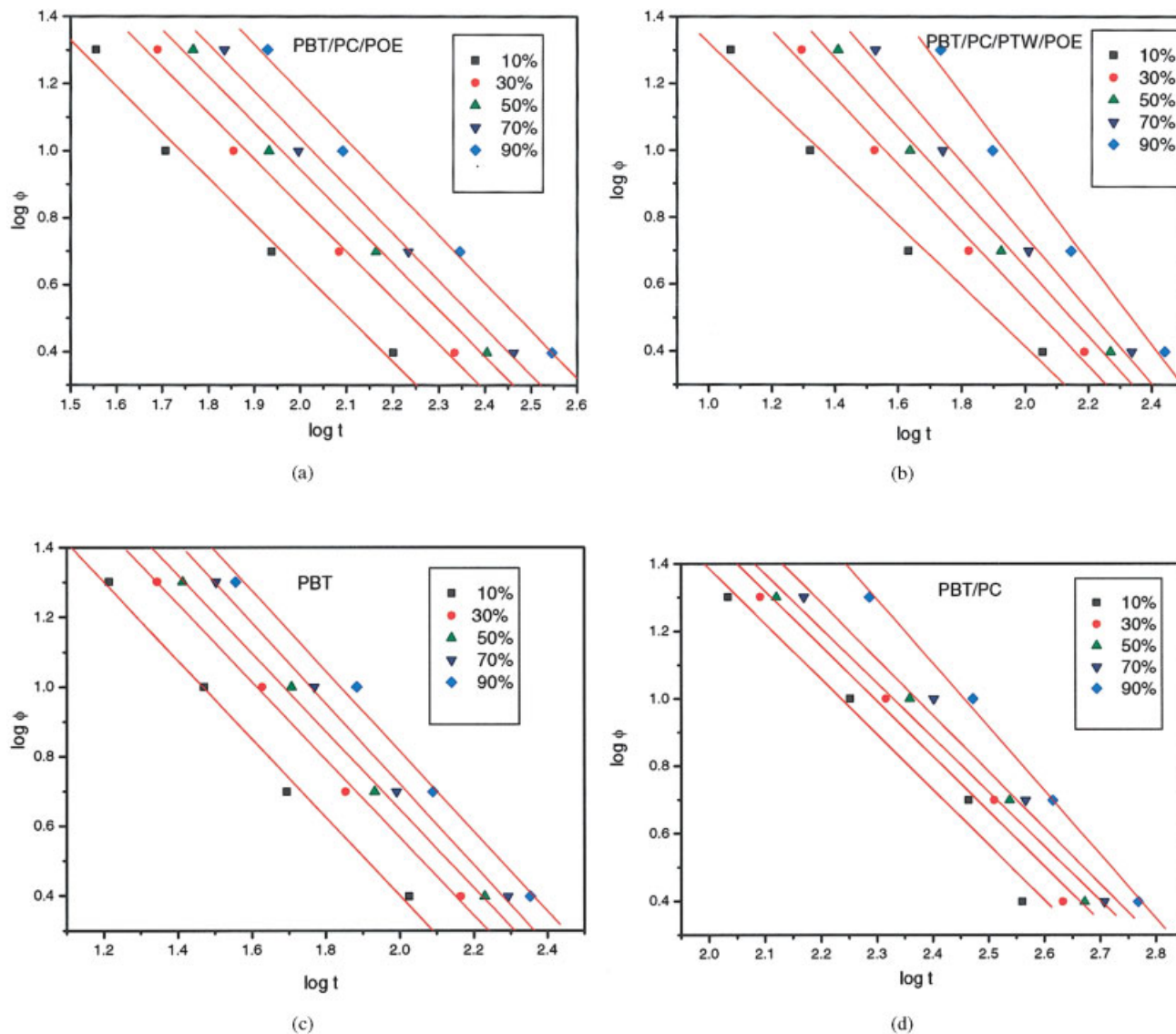


Figure 6 Plots of $\log \Phi$ versus $\log t$ for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Nonisothermal Crystallization Kinetics Parameters from Combination of Avinmi-Ozawa Equation for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE Blends

Samples	X_t (%)				
	10	30	50	70	90
PBT					
$\log F(t)$	2.65	2.80	2.89	3.03	3.11
a	1.12	1.11	1.12	1.15	1.15
PBT/PC					
$\log F(t)$	4.66	4.74	4.75	4.95	5.64
a	1.63	1.63	1.61	1.66	1.70
PBT/PC/POE					
$\log F(t)$	3.38	3.60	3.72	3.85	4.01
a	1.37	1.38	1.39	1.41	1.42
PBT/PC/PTW/POE					
$\log F(t)$	2.23	2.56	2.73	2.95	3.41
a	1.00	1.00	1.04	1.10	1.24

grams are shown in Figure 3(b). Table I gives a summary of the nonisothermal crystallization parameters according to the normalized DSC thermograms. As seen in Figure 3(a), only a single crystallization peak can be observed. T_p values of PBT in PBT/PC/POE and PBT/PC/PTW/POE blends are higher than that of PBT in PBT/PC, but lower than that of pure PBT. The $T_{\text{onset}} - T_p$ value of PBT/PC is the biggest. It is because that the incorporation of PC inhibits the crystallization of PBT in the blends.¹⁷ However, the addition of the POE into PBT/PC blend decreases the $T_{\text{onset}} - T_p$ value of PBT in PBT/PC/POE blend, and the addition of both the PTW and the POE further decreases the $T_{\text{onset}} - T_p$ value of PBT in PBT/PC/PTW/POE blend.

The rate of nucleation (S_i) and the width at half-height of the exotherm peak (ΔW) at a given cooling

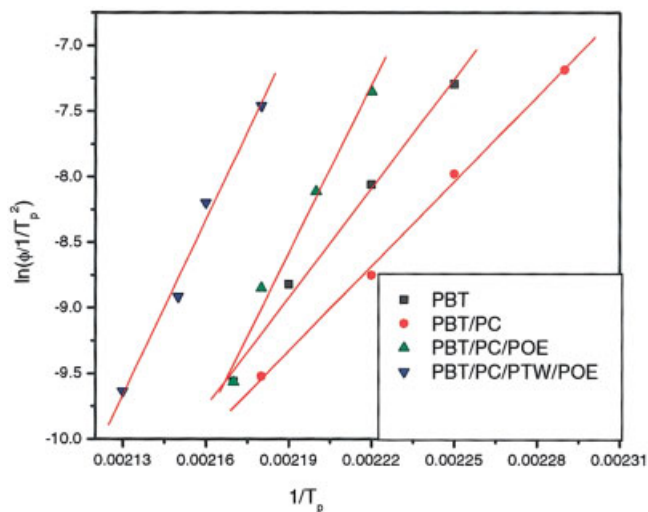


Figure 7 Kissinger plots for evaluating nonisothermal crystallization activation energy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rate are also listed in Table I. As can be observed, S_i values of the PBT/PC/POE and PBT/PC/PTW/POE blends have higher rates of nucleation than that of the PBT/PC blend. With respect to the crystallite size distribution, ΔW values of the PBT/PC/POE and PBT/PC/PTW/POE blends are smaller than that of PBT/PC blend. The results show that the POE particles in PBT/PC/POE and PBT/PC/PTW/POE blends can act as effective nucleating agents, enhancing the crystallization of PBT in the PBT/PC/POE blend. The smaller POE particles, because of the presence of PTW, result in an increase in the number of nucleating agents and further increase the crystallization rate of PBT in the PBT/PC/PTW/POE blend.

Figure 4 shows Heat flow as a function of temperature during nonisothermal crystallization at different cooling rates by DSC for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. As can be seen from the Figure, the crystallization of PBT could be carried out at lower temperature with increasing cooling rate for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends.

Considering the effect of cooling rate on the nonisothermal crystallization, Ozawa²⁸ extended the Avrami theory from isothermal crystallization to nonisothermal crystallization by assuming that the nonisothermal crystallization process was composed of infinitesimally small isothermal crystallization steps. According to Ozawa theory, the relative crystallinity $C(T)$, at temperature, can be calculated as follows:

$$C(T) = 1 - \exp[-K_c/\Phi^m] \quad (1)$$

where K_c is the cooling function related to the all over crystallization rate, and m is the Ozawa exponent that

depends on the dimension of crystal growth. Similarly, eq. (1) can be changed to its linear form:

$$\log[-\ln(1 - C(T))] = \log K_c - m \log \Phi \quad (2)$$

If this model correctly describes the nonisothermal crystallization kinetics of the samples, the graphic representation of $\log[-\ln(1 - C(T))]$ as a function of $\log \Phi$ will generate a straight line, from which K_c and m can be calculated.

Figure 5 illustrates the plots of $\log[-\ln(1 - C(T))]$ as a function of $\log \Phi$. Clearly, no straight lines are observed, indicating the failure of the Ozawa model to provide an adequate description of crystallization in PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. It is likely to the dynamic process of nonisothermal crystallization. If the cooling rates vary in a large range, large amount of crystallization occurs as a results of secondary processes, leading to the deviation from the straight lines.

It is evident that in several cases both the Avrami equation and the Ozawa equation are inadequate in analysis of nonisothermal crystallization of the polymers. Several semitheoretical mathematical models based on the Avrami equation have been proposed in the literature.^{29–31} Lou and Mo³² proposed a novel kinetics equation by combining Avrami and Ozawa equation to describe exactly the nonisothermal crystallization process. On the basis of the following assumption: the crystallinity is correlated to both the cooling rate and the crystallization time, and consequently for particular crystallinity these two parameters can be derived by combining the Avrami and Ozawa equations. The Avrami equation includes X_t and t , and the Ozawa equation includes $C(T)$ and Φ . Furthermore, the relationship of t , T , and Φ can be expressed as follows:

$$t = (T_i - T)/\Phi \quad (3)$$

where T_i is the temperature at which the crystallization begins ($t = 0$), T is the temperature at t , and Φ is the cooling rate. The Avrami equation in double-logarithmic form:

TABLE III
Crystallization Activation Energy from Eq. (6) for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE Blends

Samples	ΔE (kJ/mol)
PET	230.9
PBT/PC	219.5
PBT/PC/POE	213.2
PBT/PC/PTW/POE	370.9

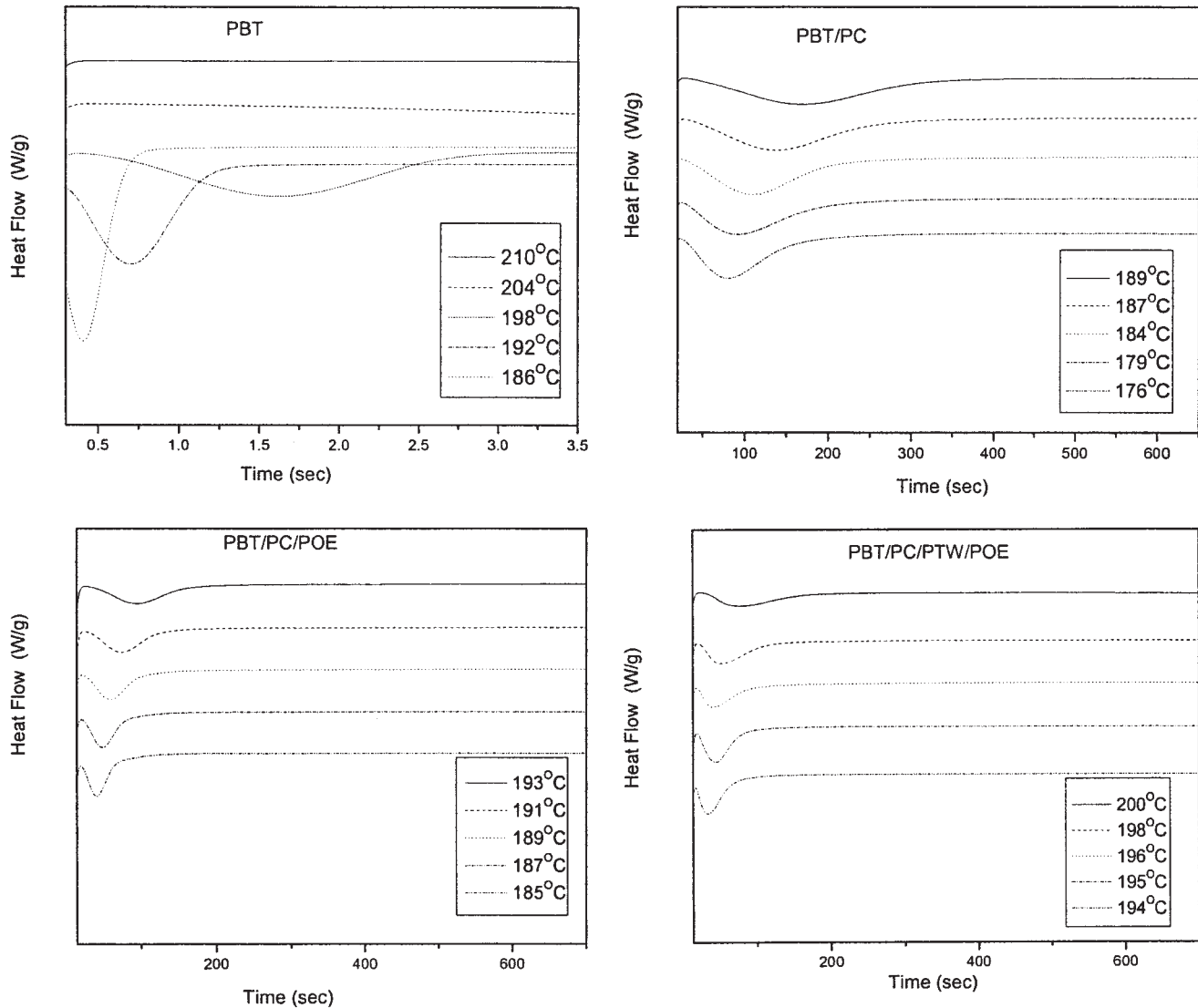


Figure 8 Heat flow as a function of time during isothermal crystallization at different crystallization temperature by DSC for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends.

$$\log[-\ln(1-X_t)] = \log Z_t + n \log t \quad (4)$$

Thus, connecting eqs. (2)–(4), the following equation can be obtained at a given crystallinity degree:

$$\log \Phi = \log F(T) - a \log t$$

where $a = \frac{n}{m}$ (ratio of Avrami exponent and the

Ozawa exponent), and $F(T) = F(T) = \left[\frac{K_c}{Z_t} \right]^{\frac{1}{m}}$ means the necessary values of cooling rate to reach a defined degree of crystallinity at unite crystallization time. According to eq. (5), at a given degree of crystallinity, the plot of $\log \Phi$ as a function of $\log t$ gives a straight line, and $\log F(T)$ and a are determined from the intercept and slope.

Figure 6 presents plots of $\log \Phi$ versus $\log t$ at various degree of crystallinity as indicated for PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. $F(T)$ and a derived from the intercept and slope of the plots are listed in Table II. The deviation of the values of a for PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends is very small, indicating that eq. (5) can successfully describe the nonisothermal crystallization of PBT in PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. As can be seen in Table II, the values of $F(T)$ increase with increasing relative crystallinity, indicating that at an unite crystallization time, a higher cooling rate should be required to obtain a higher degree of crystallinity, nevertheless, the values of the parameter a are almost constant. As can be seen in Table II, to defined degree of crystallinity, PBT/PC/POE blend requires smaller

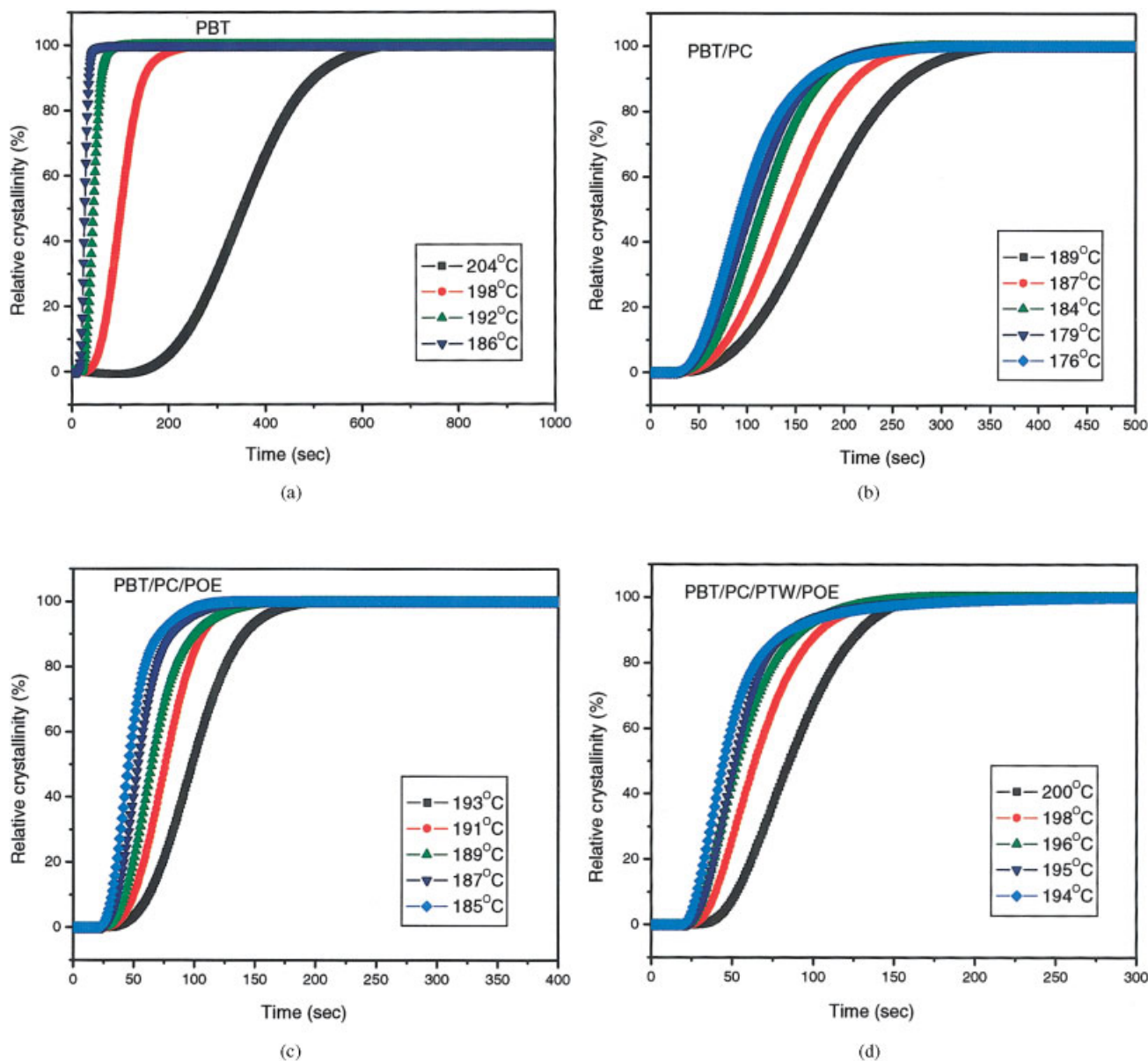


Figure 9 Relative crystallinity versus crystallization time for various crystallization temperatures from DSC thermograms of PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$F(T)$ values as compared with those of PBT/PC blend, moreover, PBT/PC/PTW/POE blend shows much smaller $F(T)$ values, which are close to those of pure PBT. The results showed the addition of POE can increase the crystallization rate of PBT in the PBT/PC/POE blend, and the addition of both PTW and POE can further increase the crystallization rate of PBT in the PBT/PC/PTW/POE blend.

By taking into account the influence of various cooling rates Φ , Kissinger³³ proposed that the crystallization activation energy could be determined by calculating the variation of the crystallization peak temperature with the cooling rate. The formula can be given as eq. (6)

$$\frac{d(\ln \Phi / T_p^2)}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (6)$$

where R is the gas constant and T_p is the crystallization peak temperature. The values of $\ln(\Phi/T_p^2)$ are plotted as functions of $1/T_p$ in Figure 7. The values of the activation energy obtained are listed in Table III. As can be seen in Table III, the ΔE of PBT/PC/PTW/POE blend is greater than that of PBT/PC/POE blend, suggesting a more difficult motion of the PBT chain segments. It is likely that high viscosity caused by the reaction between epoxide groups in PTW can react with the terminal carboxylic acid and/or hydroxyl groups of PBT in melt state, as reported by Yang et al.³⁴

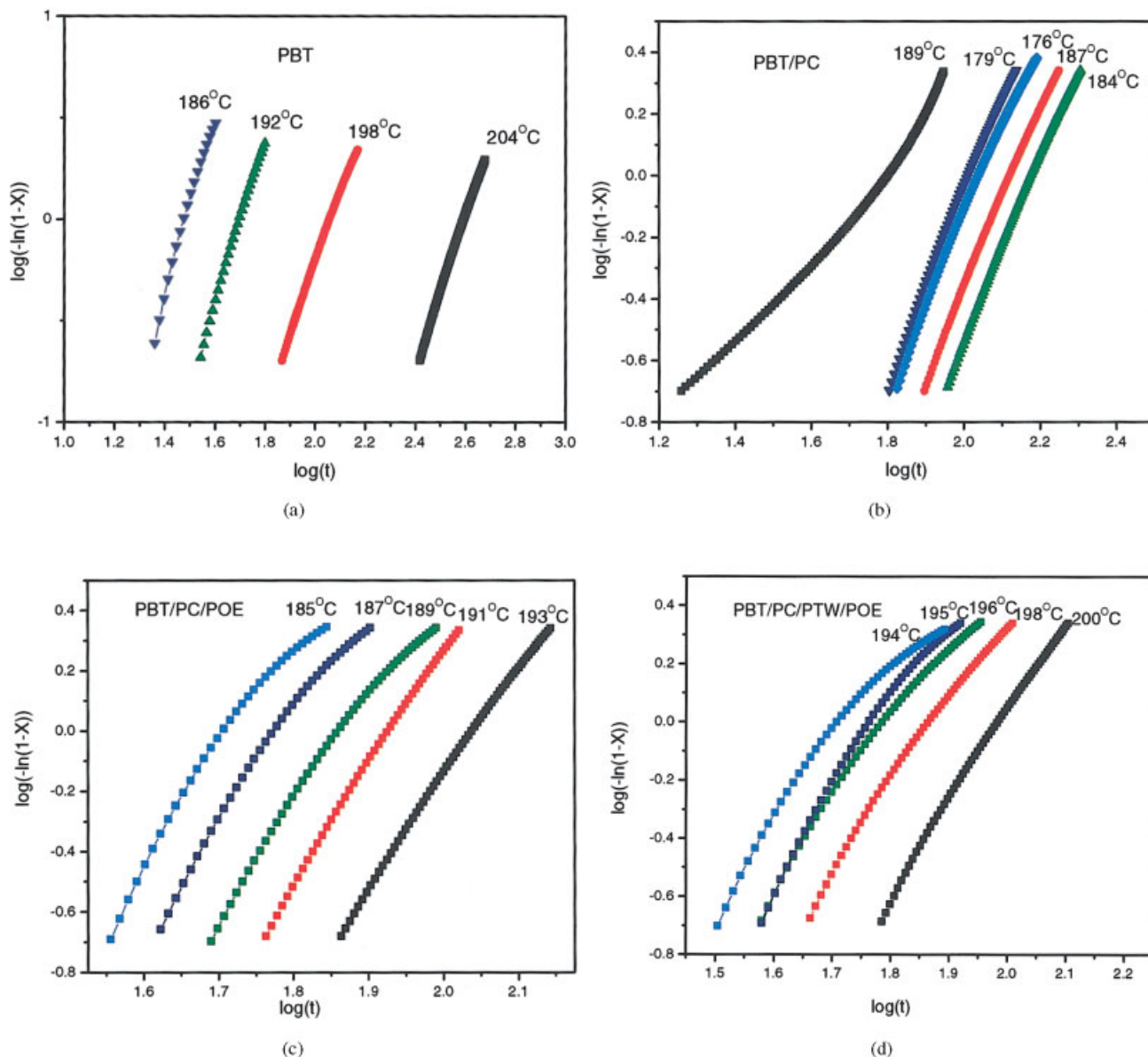


Figure 10 Plots of $\log[-\ln(1-X(T))]$ versus $\log t$ for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Isothermal crystallization analysis

Considering the importance of isothermal crystallization rate to the commercial utility of a thermoplastic polyester, an insight into the isothermal crystallization is important.

Figure 8 shows the dependence of heat flow on crystallization time at different crystallization temperature for PBT and its blends. As can be seen from the Figure 8, the crystallization exothermic peak between flatter and the time to reach the maximum degree of crystallization increases with increasing crystallization temperature.

The isothermal crystallization kinetics of a polymer can be analyzed by evaluating its degree of crystalline

conversion as a function of time at a constant temperature. In analyzing, the relative crystallinity, X_t , developed up to time t , was the ratio of the areas between the heat-time curve and the baseline of the sample^{35,36}

$$X_t = \frac{Q_t}{Q_\infty} = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^{t_\infty} \frac{dH}{dt} dt} \quad (7)$$

where Q_t and Q_∞ are the heat generated at time t and infinite time, respectively, and $\frac{dH}{dt}$ is the heat flow rate.

TABLE IV
Kinetic Parameters of PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE Blends from the Analysis of Isothermal Crystallization

Samples	T (°C)	n	$\log K(T)$	$T_{1/2}^a$ (s)	$T_{1/2}^b$ (s)
PBT	210				
	204	3.7	-3.07	5.78	5.94
	198	3.5	-1.00	1.73	1.73
	192	3.8	0.31	0.84	0.75
	186	4.0	1.25	0.44	0.45
PBT/PC	189	3.1	-1.45	2.57	2.59
	187	3.0	-1.06	1.95	1.97
	184	3.0	-1.21	2.21	2.23
	179	3.0	-0.76	1.51	1.54
	176	2.9	-0.77	1.58	1.63
PBT/PC/POE	193	3.5	-0.94	1.64	1.65
	191	3.5	-0.52	1.28	1.26
	189	3.2	-0.27	1.08	1.08
	187	3.2	0.01	0.89	0.88
	185	3.5	0.25	0.76	0.77
PBT/PC/PTW/POE	200	2.8	-0.58	1.41	1.41
	198	2.8	-0.25	1.07	1.08
	196	2.7	-0.02	0.96	0.89
	195	2.6	0.03	0.87	0.84
	194	3.0	0.22	0.75	0.75

^a Determined from Figure 9.

^b Calculated from eq. (10).

The development of the relative crystallinity with time for PBT and its blends are plotted in Figure 9. The characteristic isotherms are shifted to right along the time axis with the increasing crystallization temperature., indicating progressively slower crystallization rate. After most of the crystallization had taken place, a slow increase of crystallinity with time was observed, which could be attributed to the presence of secondary crystallization.³⁷

The degree of crystallinity against time was analyzed using the Avrami equation,³⁷⁻³⁹ which can be expressed as follows:

$$X(t) = 1 - \exp(-Kt^n) \quad (8)$$

where K is the Avrami rate constant containing the nucleation and the growth parameters, n is the Avrami exponent dependent on the mechanism of nucleation, the form of crystal growth, and the crystallization time. Equation (8) can also be converted to

$$\log[-\ln(1-X(t))] = \log K + n \log t \quad (9)$$

Plots of $\log(-\ln(1-X_t))$ versus $\log t$ are shown in Figure 10. For comparison, the regime of about 10–80% conversion in the curves for all the samples is chosen to determine the exponent n and K according to eq. (8) and presented in Table IV. The values of pure PBT, PBT/PC and its blends range from 2.8–4, and are higher than the values reported in the literature.⁴⁰ The

higher value of n is likely a reflection of memory effects associated with the processing of polymers, which were extruded using a twin-screw extruder following injection. The similar phenomena in nylon 6 nanocompositions were observed by Fornes and Paul.⁴¹

Another important parameter is the half-time of crystallization $t_{1/2}$, which is defined as the time at which the extent of crystallization is 50%. It can be conveniently extracted from the plots of relative crystallinity $X(t)$ versus time t in Figure 9. The relation between $t_{1/2}$ and K can be expressed

$$K = \frac{\ln 2}{t_{1/2}^n} \quad (10)$$

Using eq. (10) the theoretical values of $t_{1/2}$ can be calculated, by taking the K value from the experimental data. The values of $t_{1/2}$ derived both from experimental data and eq.(10) are listed in Table IV. As can be seen in Table IV, the values of $t_{1/2}$ derived from eq.(10) agree well with those obtained from the experimental plots. The $t_{1/2}$ is directly employed to describe the rate of crystallization. The greater the value of $t_{1/2}$ the lower the rate of the crystallization. As shown in Table IV, the addition of POE to the PBT/PC blend decreases the values of $t_{1/2}$, and the addition of PTW to the PBT/PC/PTW/POE blend further decreases values of $t_{1/2}$, indicating that the PBT/PC/PTW/POE

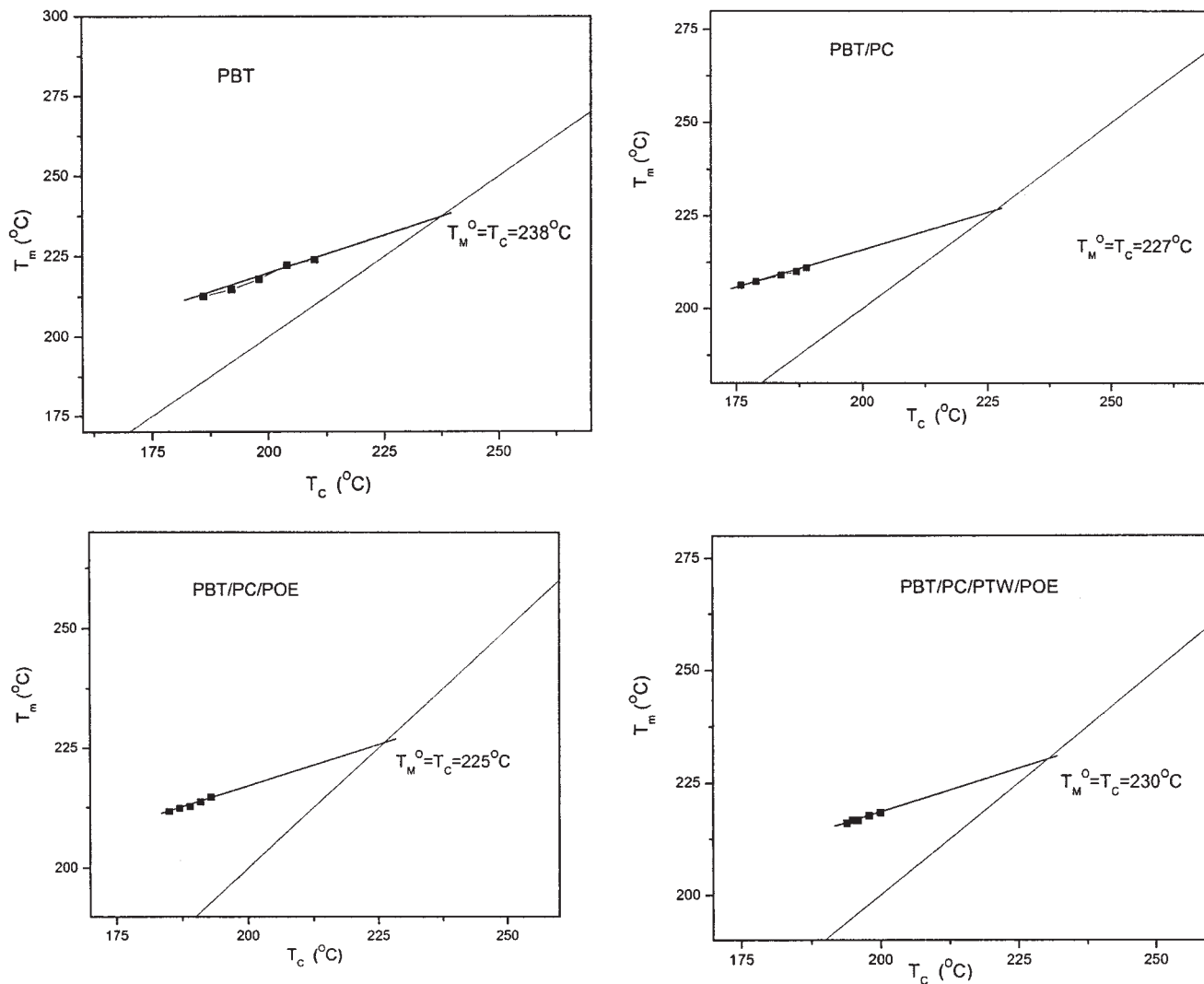


Figure 11 Melting temperature as a function of crystallization temperatures for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends.

blend has a greater rate of crystallization than those of PBT/PC, PBT/PC/POE blends.

Estimation of the correct equilibrium melting points (T_m^0) is an important task, since the analysis of the growth kinetics is very sensitive to the values of T_m^0 used in calculation. The T_m^0 was determined using the method suggested by Hoffman and Weeks.⁴² After crystallization at T_c , polymers were reheated at a rate of $20^\circ\text{C}/\text{min}$. Two melting peaks can be exhibited in pure PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. The low temperature peak is associated with the melting of dominant lamella and represents melting of crystallization formed at the crystallization temperature.⁴³ The low temperature peak has been used for determination of equilibrium melting point of PBT. It was possible to calculate T_m^0 by the plotting of T_c versus T_m in Figure 11, and to observe the intersection of this line with another line with a slope equal to 1. The T_m^0 for PBT was found to be

238°C . The reported values of equilibrium melting points vary between 236°C and 249°C .^{44–47}

The crystallization kinetics were analyzed on the basis of Lauritzen-Hoffman theory,⁴⁸ which can be expressed as follows

$$\ln K(T) + \frac{n\Delta F}{RT_c} = \ln A_n - \frac{nK_g}{fT_c\Delta T} \quad (11)$$

where ΔT is equal to $T_m^0 - T_c$, A_n can be taken as constants, ΔF is the activation energy for the transport process at the liquid–solid interphase and can be calculated with high precision from the Williams-Landel-Ferry (WLF) Equations,⁴⁹ which is given by the following expression:

$$\Delta F = \Delta F_{\text{WLF}} = \frac{C_1 T_c}{C_2 + T_c - T_g} \quad (12)$$

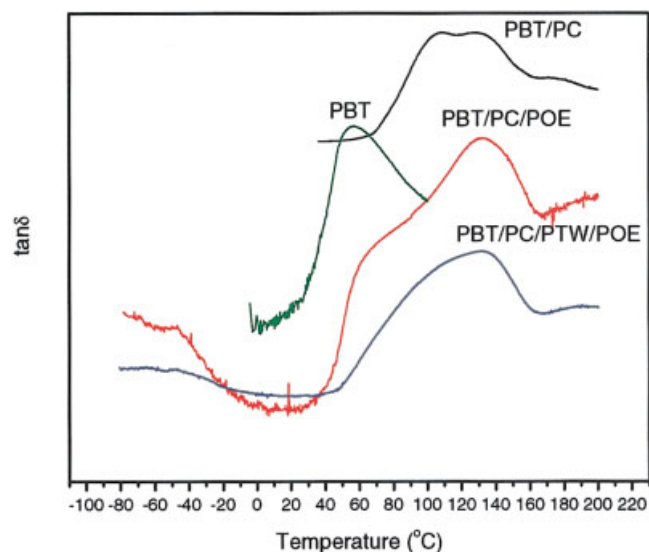


Figure 12 The DMTA spectra of PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Parameters In A_n and k_g in Eq. (11) for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE Blends

Samples	$\ln A_n$	k_g
PBT	51.0	388.1
PBT/PC	29.6	143.1
PBT/PC/POE	35.6	178.7
PBT/PC/PTW/POE	41.8	288.5

where C_1 and C_2 are constants and their values are assumed to be 17.24 and 51.6 kJ/mol.

Thus, drawing a straight line of the left-hand side of eq.(11) against $n/T_c(\Delta T)f$ will give a slope of $-K_g$. Using the obtained values of T_m in the present case and the obtained values of T_g by DMTA analysis ($T_g = 50, 80, 75,$ and 80°C , respectively, for PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends) (Fig. 12) the obtained $\ln A_n$ and K_g values are listed in Table V.

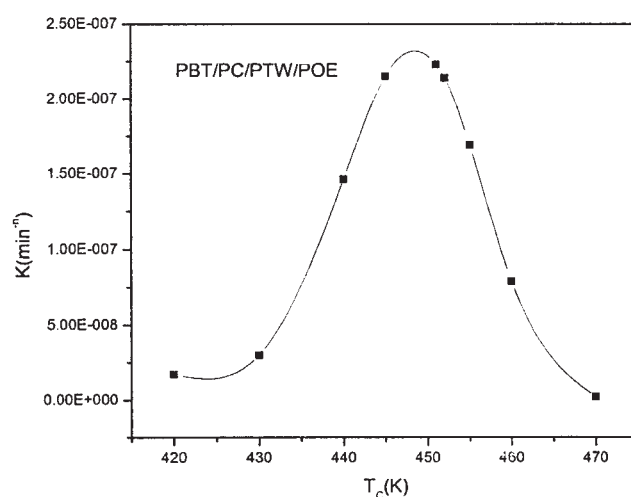
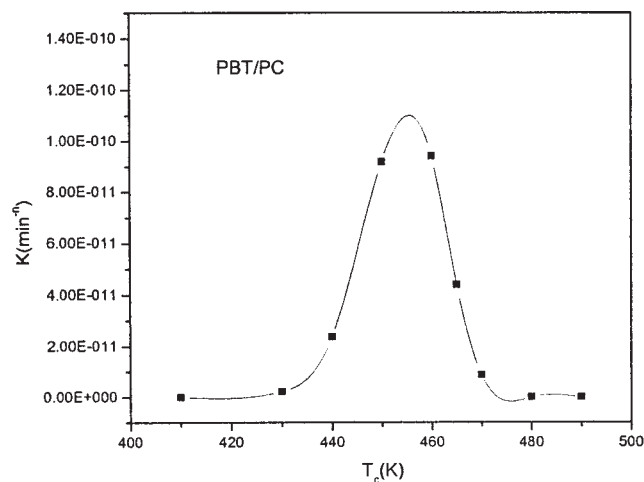
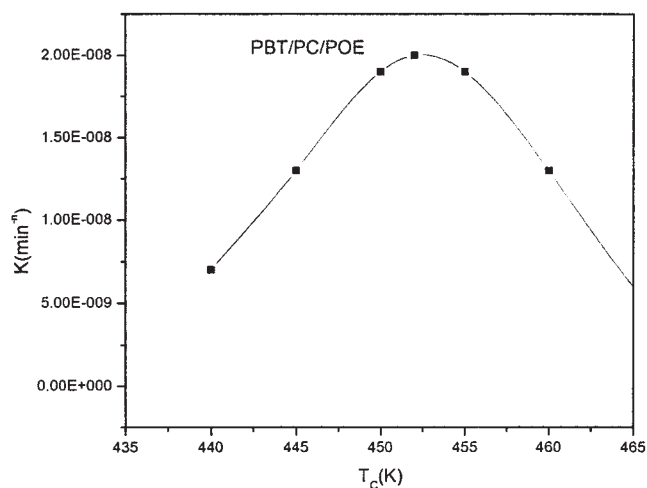
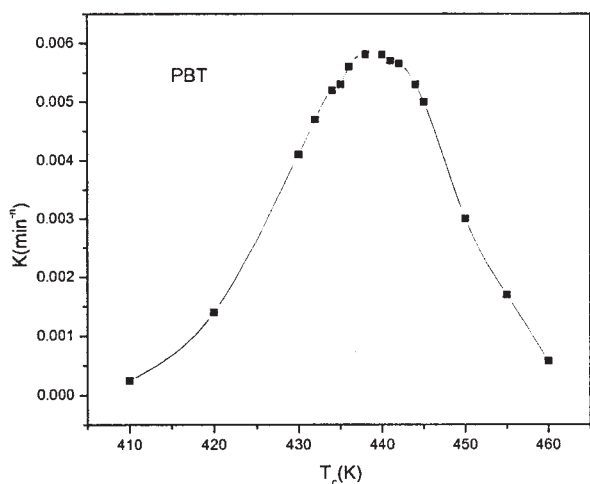


Figure 13 The crystallization rate constant K as a function of crystallization temperature for PBT and PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends.

The dependence of the crystallization rate constant K on temperature is shown in Figure 13. The K values for the PBT/PC/POE blend and the PBT/PC/PTW/POE blend are higher than those for the PBT/PC blend, suggesting that the addition of POE can improve the crystallization rate of PBT in the PBT/PC/POE blend, and the addition of both PTW and POE can further improve the crystallization rate of PBT in the PBT/PC/PTW/POE blend, as can also be observed in the nonisothermal process. The fastest rate of crystallization could be found at 440, 460, 450, and 442 K, respectively, for PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends.

CONCLUSIONS

For the nonisothermal crystallization for pure PBT and PBT/PC, PBT/PC/POE, PBT/PC/PTW/POE blends, the Ozawa equation is not suitable while the combined Avrami and Ozawa equation can be used to describe the nonisothermal crystallization process. The Kissinger method can be employed to obtain the activation energy. The activation energy values were found to be 230.9, 219.5, 213.2, and 370.9 kJ/mol of pure PBT and PBT/PC, PBT/PC/POE, PBT/PC/PTW/POE blends, respectively.

For the isothermal crystallization, Avrami equation can be used to obtain the values of the Avrami exponent n and the Avrami rate constant K for pure PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends. The values of n for pure PBT, PBT/PC, PBT/PC/POE, and PBT/PC/PTW/POE blends are 3.8, 3.0, 3.2, and 2.8, respectively. In addition, the crystallization rate of PBT in pure PBT and its blends increases in following order: PBT/PC < PBT/PC/POE < PBT/PC/PTW/POE < PBT.

Based on the above demonstration, it is clear that POE acts as nucleation agent for the crystallization of PBT in PBT/PC blends. Incorporation of POE can greatly influence the crystallization rate of PBT in PBT/PC/POE and PBT/PC/PTW/POE blends. The facts are related to their morphology. The POE particles, which disperse in large sizes in the PBT/PC/POE blends, enhance the crystallization of PBT. The POE particles, which disperse in small sizes because of the presence of PTW in the blends, further enhance the crystallization of PBT. The results are confirmed by SEM.

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