Crystalline and Thermal Behavior of Poly(ethylene terephthalate)/Polyphenoxy Blends

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ABSTRACT: Poly(ethylene terephthalate) (PET)/polyphenoxy blends were prepared by melt blending. Crystalline and thermal behaviors of PET/polyphenoxy blends were verified by use of DSC. The experiment results show that the initial temperature, peak temperature, and ending temperature of cold crystallization increase with increasing phenoxy content. On the contrary, the onset melting temperature, finishing melting temperature, and peak temperature in the first heating and the secondary heating processes decrease with increasing phenoxy content. The crystallization enthalpy and melting enthalpy, as well as the crystallization rate, decrease with increasing phenoxy content. Avrami exponents of the blends are slightly higher than that of pure PET and almost independent of phenoxy content. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 878–885, 2005

Key words: poly(ethylene terephthalate) (PET); phenoxy; blends; thermal properties; crystallization

INTRODUCTION

Blending two or more thermoplastics is a useful way to obtain new materials with desired properties.[1–8] The majority of blends are immiscible; that is, they possess a phase-separated morphology. Immiscible polymer blends often present poor mechanical properties relative to their components because of unfavorable interaction between molecular segments at the interface, that is, a large interfacial tension, which leads to poor control of morphology during melt mixing and poor interfacial adhesion or stress transfer in the solid state. Although most polymers are immiscible and even incompatible, useful blends with good properties are achieved through the formation of special morphologies. The morphologies of immiscible polymers are affected by blending conditions, interfacial tension between components, special interactions such as possible covalent bond or hydrogen bond, and the viscosity of components.

Among immiscible blends, we chose poly(ethylene terephthalate) (PET) and polyphenoxy as the blend components. PET is mainly used for films, synthetic fiber, recording tapes, and bottles. Thus, PET is a contributor of substantial amounts of postconsumer household waste, causing serious waste-disposal problems. Several studies about PET-blend systems have been reported. High-density polyethylene (HDPE) grafted with blocked isocyanate group (HDPE-*g*-BHI) was used as a reactive compatibilizer for an immiscible HDPE/PET blend.[9] The blend system of bisphenol-A polycarbonate (PC)/PET was compatibilized with a transesterification product.[10] It was found that after a long time of transesterification between PET and PC (50/50, wt %), the resultant product (i.e., a random copolymer) is miscible with individual homopolymers of PC and PET. A truly miscible ternary blend composed of poly(ε-caprolactone) (PCL), poly(benzyl methacrylate) (PBzMA), and poly(vinyl methyl ether) (PVME), was reported.[11] Miscibility with phase homogeneity in a wide composition range was demonstrated.

In the present work PET/polyphenoxy blends were prepared by melt blending. Crystalline, thermal behaviors of PET/polyphenoxy blends were verified. Also the experiments on isothermal and nonisothermal crystalline kinetics were carried out. The influences of blend composition on properties were examined.

EXPERIMENTAL

Materials

PET was supplied by Shanghai Dacron Factory (China) with a relative viscosity 0.7. Phenoxy was from Totocasei Corp. (Tokyo, Japan).

Preparation of PET/phenoxy blends

A Brabender-like apparatus was used to prepare PET/phenoxy blends with a roller speed of 64 rpm for 10

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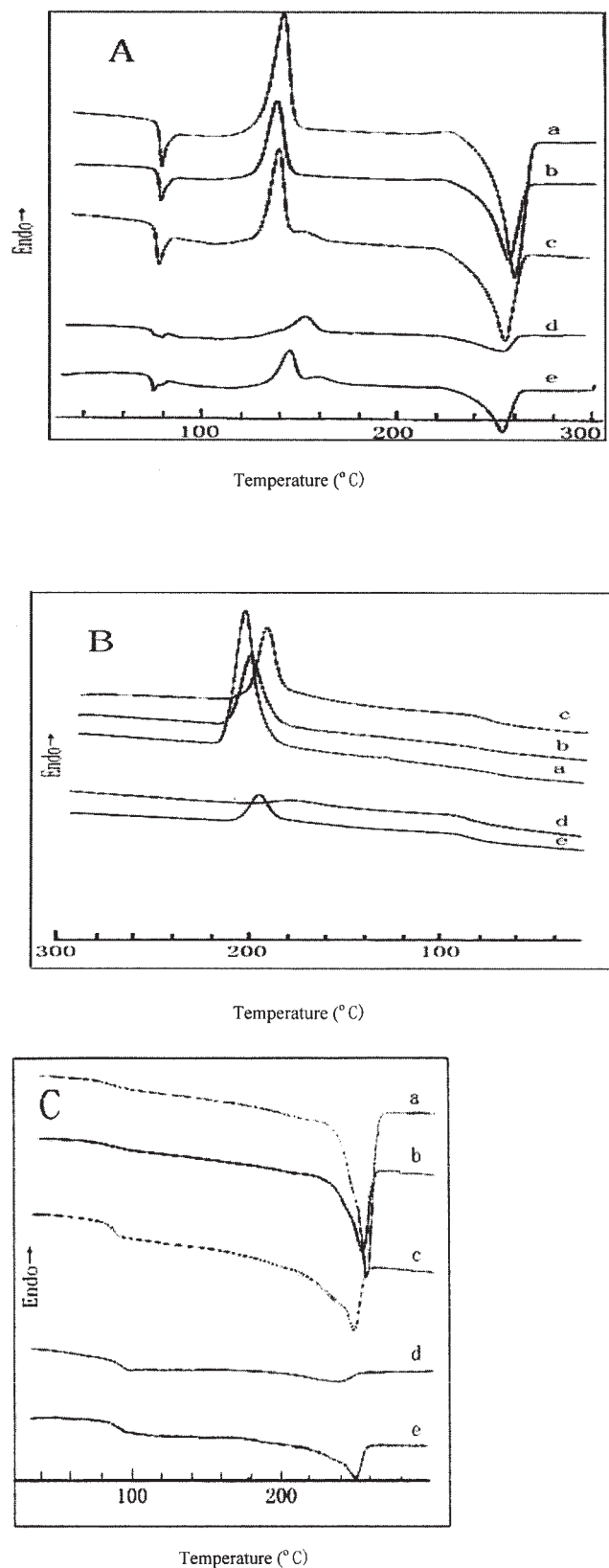
Figure 1 Thermograms of blends: (A) first heating; (B) cooling; (C) secondary heating. PET/Phenoxy: (a) 100/0; (b) 90/10; (c) 70/30; (d) 70/30; (e) 50/50.

min. PET and phenoxy were dried in a vacuum oven at 80°C for 24 h before melt mixing.

Characterization

Crystallization and melting behaviors were validated by using DSC [model DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) and model DSC 321e (Mettler Toledo, Zurich, Switzerland)] at a speed of 10°C/min. Isothermal crystallization dynamics was measured by using a Perkin–Elmer DSC-7 apparatus in the following program: the sample was first heated to
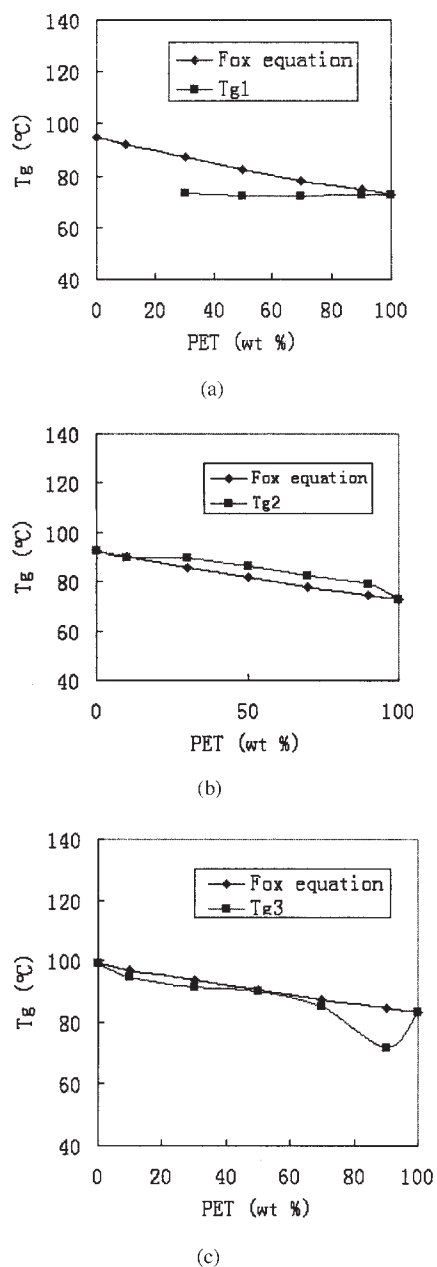
Figure 2 T_g versus composition of blends: (a) T_{g1}; (b) T_{g2}; (c) T_{g3}.

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TABLE I
DSC Results[a]

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	T_{g1}	T_{c1}	T_{m1}	T_{c2}	T_{g2}	T_{g3}	T_{m2}
PET	72.95	136.26	257.26	209.23	72.91	82.99	254.79
PET90	72.81	133.81	253.82	205.49	78.79	71.51	251.85
PET70	72.24	135.10	253.20	197.57	82.41	85.10	247.27
PET50	72.47	143.16	252.83	197.98	86.26	90.19	249.36
PET30	73.48	150.82	252.59	179.24	89.93	91.45	236.44

	T_{c1}		T_{m1}		T_{c2}		T_{m2}	
	Onset	Endset	Onset	Endset	Onset	Endset	Onset	Endset
PET	126.79	142.56	243.79	264.94	217.95	199.18	243.69	260.42
PET90	125.57	140.78	239.52	262.91	214.93	193.22	237.81	258.03
PET70	127.67	140.71	241.09	260.52	206.11	188.62	231.15	253.58
PET50	133.50	149.96	240.81	261.09	207.10	187.56	233.51	255.34
PET30	138.38	159.69	227.56	260.80	199.21	151.15	198.98	251.38

	ΔH_{c1}	ΔH_{m1}	ΔH_{c2}	ΔH_{m2}
PET	37.19	64.37	53.94	49.10
PET90	30.87	54.44	45.20	39.39
PET70	30.23	54.62	37.75	41.61
PET50	41.98	52.66	35.45	48.34
PET30	38.50	31.24	28.00	37.50

[a] $\Delta H_0 = 125.52$ J/g.

300°C and maintained at this temperature for 5 min, and then cooled to the setting temperature. Nonisothermal crystallization dynamics was performed using Mettler Toledo DSC 321e equipment with almost the same program but cooled at a setting rate.

RESULTS AND DISCUSSION

Figure 1 shows DSC thermograms of different composition blends with heating, cooling, and secondary heating programs. When the PET content is not <30%, glass transition (T_{g1}) appears near 73°C and the melting peak appears near 253°C in the first heating process and, in addition, there is a cooling crystallization peak (T_{c1}) between 136 and 150°C. The cooling experiment shows a cooling crystallization peak (T_{c2}) between 136 and 150°C and a glass transition (T_{g2}) between 83 and 99°C. In the secondary heating process, the cooling crystallization peak disappears and glass transition (T_{g3}) is >T_{c1}.

Because there is strong interaction between PET and phenoxy, the blend shows only one T_{g1}, the value of which is related to its heating history. When the PET content is not <30%, glass transitions of the samples are very similar to that of pure PET and generally do not change with blend composition [Fig. 2(a)]. T_{g2}, obtained from the cooling curve, shows a positive deviation from the Fox equation [Fig. 2(b)]. T_{g3}, obtained in the secondary heating process, corresponds with the calculated value obtained by the Fox equation [Fig. 2(c)].

The crystallization temperature range of crystalline polymer is between T_g and T_m. Although the glass-transition temperature of the blend is much lower than the PET crystallization temperature, phenoxy exerts a strong influence on PET crystalline behavior because of the strong interaction between PET and phenoxy. Table I shows that the onset temperature of cooling crystallization is about the same as that of pure PET when the PET content is higher. Peak temperature and end crystallization temperature both increase with increasing phenoxy content and the crystallization temperature range becomes wider.
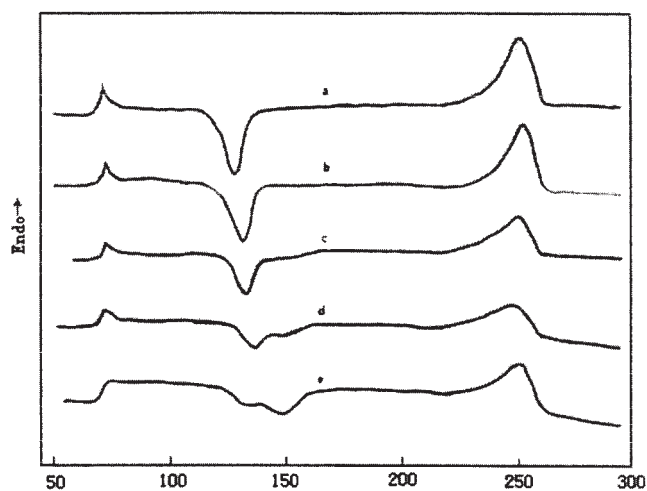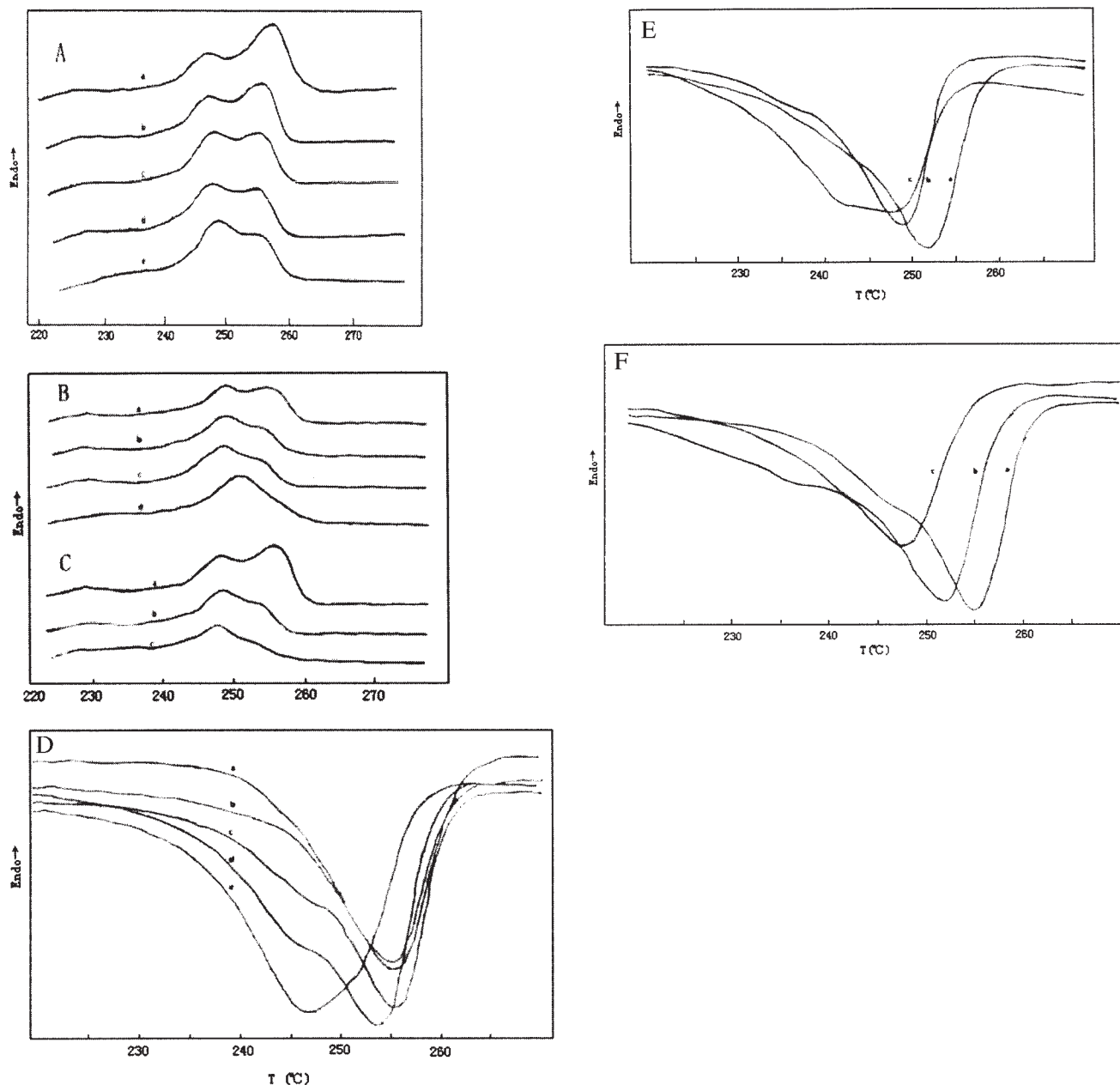

Figure 3 Heating curves of blends. PET/Phenoxy: (a) 100/0; (b) 90/10; (c) 70/30; (d) 50/50; (e) 30/70.

Figure 4 (A) Heating curves of PET at isothermal crystallization: (a) 218°C; (b) 219°C; (c) 220°C; (d) 221°C; (e) 222°C. (B) Heating curves of PET/phenoxy (90/10) at isothermal crystallization: (a) 217°C; (b) 218°C; (c) 219°C; (d) 220°C; (e) 221°C. (C) Heating curves of PET/phenoxy blend at isothermal crystallization. PET/Phenoxy: (a) 100/0; (b) 90/10; (c) 70/30. (D) Cooling curves of PET at nonisothermal crystallization. Cooling speed (°C/min): (a) 50; (b) 20; (c) 10; (d) 5; (e) 2. (E) Cooling curves of PET/phenoxy (90/10) at nonisothermal crystallization. Cooling speed (°C/min): (a) 20; (b) 10; (c) 5. (F) Cooling curves of PET and its blend at nonisothermal crystallization. PET/Phenoxy: (a) 100/0; (b) 90/10; (c) 70/30; Cooling speed: 10°C/min.

With increasing phenoxy content and degree of supercooling the onset temperature of melt cooling crystallization, peak temperature, and finishing crystallization temperature increase and the phenomenon of widening crystallization temperature range is more obvious than that in cooling crystallization. The onset melting temperature, finishing melting temperature, and peak temperature in the first heating and the secondary heating processes decrease with increasing

phenoxy content, and the melting temperature range widens. Melting heat (ΔH_{m1}) and crystallization heat (ΔH_{c2}) decrease with increasing phenoxy content. When the phenoxy content is 30%, the sample's heating curve presents two cooling crystallization peaks. With increasing phenoxy content the high temperature peak becomes more pronounced, but the peak position does not change (Fig. 3). Double melting peaks appear in the heating curve of the isothermal

crystallization sample. The high-temperature melting peak of the sample crystallized at the same temperature shows the same phenomenon, although not as obvious as that of pure PET, and the peak strength becomes weaker with increasing phenoxy content. The high-temperature peak of the sample with the same composition ratio becomes weaker with increasing crystallization temperature (Fig. 4).

DSC heating curves of nonisothermal crystallization samples are shown in Figure 4(D)–(F). With increasing cooling speed or phenoxy content, the melting peak moves to a high temperature. When the cooling speed is <10°C/min either PET or PET/phenoxy (90/10) presents one shoulder peak. The relative position of the shoulder peak to the main peak is related to cooling speed. With increasing cooling speed the shoulder peak at low temperature gradually becomes smaller. When the cooling speed is the same, the shoulder peak becomes more prominent with increasing phenoxy content (Fig. 4F).

The above results demonstrate that phenoxy has a substantial effect on PET crystallization behavior because of the strong intermolecular interaction between PET and phenoxy. PET has an influence not only on the crystalline temperature of the PET blend but also on its crystalline perfection, which means that the crystalline structure becomes less perfect with increasing cooling crystallization temperature and decreasing crystallization temperature. Figure 5 shows the curves of relative crystalline fraction (X) versus time (t) at isothermal crystallization. The crystalline speed of PET and its blend decreases with increasing crystalline temperature over the investigated temperature range. The crystalline speed of the sample crystallized at the same temperature is slowed with increasing phenoxy content. From Table II it is clearly seen that PET crystalline dynamic constant (k) becomes smaller with increasing phenoxy content and crystalline temperature, although the half-time of crystallization $t_{1/2}$ increases with increasing phenoxy content and crystalline temperature. The Avrami exponent of the blend (n) is slightly higher than that of pure PET and generally is not dependent on phenoxy content.

Figure 6 shows the relative crystalline fraction (X) versus time (t) curve of PET/phenoxy (90/10), (70/30) blends at nonisothermal crystallization. Time t can be derived from the following equation:

$$t = (T_0 - T)/V \qquad (1)$$

where T_0 is the initial crystalline temperature, T is the temperature at crystalline time t, and V is the cooling speed. From this equation it can be established that the faster the cooling speed, the less the time for complete crystallization.

The dynamic behavior of isothermal crystallization can be described by an Avrami equation,[12] as follows:
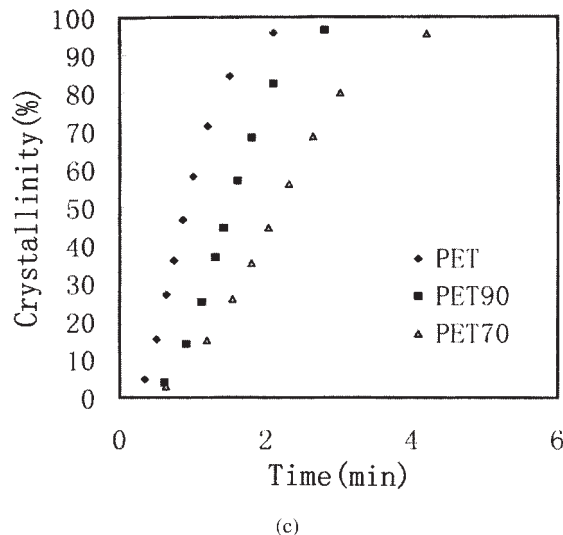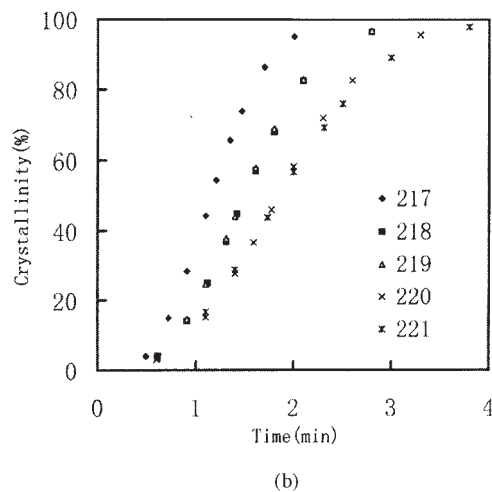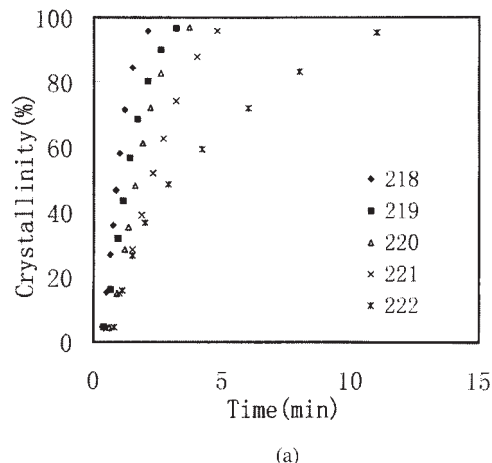

(a)

(b)

(c)

Figure 5   (a) Relation of crystallinity to time for pure PET. (b) Relation of crystallinity to time for PET/phenoxy (70/30). (c) Relation of crystallinity to time for blends at 219°C.

$$1 - X_t = \exp(-kt^n) \qquad (2)$$

where n is the Avrami exponent and k is the crystalline rate constant.

TABLE II
Crystallization Kinetic Parameters of PET/Phenoxy Blend

	$t_{1/2}$			n			$k(\text{min}^{-n})$		
	PET	PET90	PET70	PET	PET90	PET70	PET	PET90	PET70
218°C	1.05	1.45	2.15	2.0	2.5	2.5	0.79	0.48	0.11
219°C	1.30	1.50	2.45	1.9	2.7	2.6	0.42	0.36	0.09
220°C	1.85	2.23	2.70	2.0	2.6	2.6	0.26	0.13	0.06
221°C	1.65	1.85	2.50	1.9	2.6	2.7	0.17	0.10	0.02

By plotting the curve of $\log[-\ln(1 - X_t)]$ versus $\log(t)$ we find that the PET/phenoxy (90/10) blend, crystallized at different cooling speeds, presents a group of straight lines with about the same slopes at the beginning of crystallization, which means that the nucleating process and growing mechanism are basically free of the influence of cooling speed and blend composition ratio. Although the curve shape of PET/phenoxy (70/30) is quite complex in the later period, the straight-line portion can still be seen in the previous period. The Avrami exponent n and crystalline rate constant k can also be obtained from straight-line slopes and intercepts.

The rate constant K in the Avrami equation was revised with cooling speed by Jeziorny[13]:

$$\log K_c = \log K/V \tag{3}$$

The n value, revised rate of crystallization K_c, and half-time of crystallization $t_{1/2}$, obtained from Figure 7, are shown in Table III. It can be seen that the n value of PET in the nonisothermal crystallizing process is between 3 and 3.4, higher than the n value (~ 2) in the isothermal crystallizing process. The n values of blends are slightly higher than those of pure polymers. The changing trend is the same with the isothermal crystallizing process, that is, K_c decreases and t_t increases with decreasing cooling rate.

Considering the influence of cooling rate on crystallization behavior, Ozawa[14] extended the Avrami equation to the nonisothermal crystallizing process and derived the following equation:

$$1 - C(T) = \exp[-K(T)/V_m] \tag{4}$$

where $C(T)$ is the relative degree of crystallinity at temperature T, m is the Ozawa exponent, V is the cooling rate, and $K(T)$ is the kinetic parameter. From the plot of $\log\{-\ln[1 - C(T)]\}$ versus $\log V$, a straight line would be obtained with $-m$ as slope and $\log K(T)$ as intercept. Mo[15] derived a kinetic parameter $F(T)$ related to the nonisothermal crystallizing process by combining the Ozawa equation with the Avrami equation:

$$F(T) = [K(T)/K]^{1/m} \tag{5}$$

where K is the Avrami exponent. The following equation can be derived by ordering $\alpha = n/m$:

$$\log V = \log F(T) - \alpha \log t \tag{6}$$

The figure of $\log V$ versus $\log t$ is a straight line with $-\alpha$ as slope and $\log F(T)$ as intercept (Fig. 8). The values of α and $F(T)$, obtained from eq. (6), are listed in Table IV.

TABLE III
Non-Isothermal Crystallization Kinetic Parameters at Different Cooling Rates

PET/Phenoxy	V (°C/min)	n	K_c	$t_{1/2}$
100/0	50	3.00	1.18×10^{-1}	0.46
	20	3.04	3.96×10^{-2}	0.87
	10	3.26	2.19×10^{-2}	1.32
	5	3.34	2.25×10^{-3}	3.16
90/10	50	3.49	3.38×10^{-1}	0.39
	20	3.42	7.01×10^{-2}	0.66
	10	2.87	1.77×10^{-2}	1.43
	5	3.46	5.59×10^{-3}	2.33
70/30	50	3.30	7.19×10^{-2}	0.58
	20	3.62	1.90×10^{-2}	1.09
	10	4.18	3.89×10^{-3}	1.96
	5	3.58	5.78×10^{-3}	3.58

TABLE IV
α and $F(T)$ Values of PET and Its Blend at Different Degrees of Crystallization

PET/Phenoxy	X_t	$F(T)$	α
100/0	20	12.6	1.10
	40	17.0	1.23
	60	21.4	1.33
	80	26.9	1.43
90/10	20	10.5	1.02
	40	14.5	1.16
	60	17.8	1.25
	80	21.9	1.34
70/30	20	16.2	1.21
	40	22.4	1.35
	60	28.2	1.45
	80	35.5	1.55
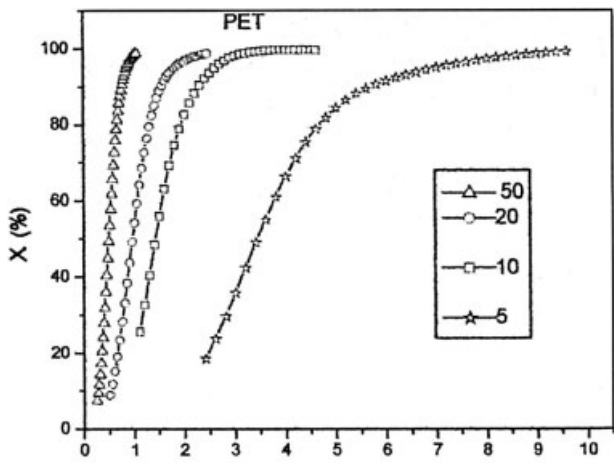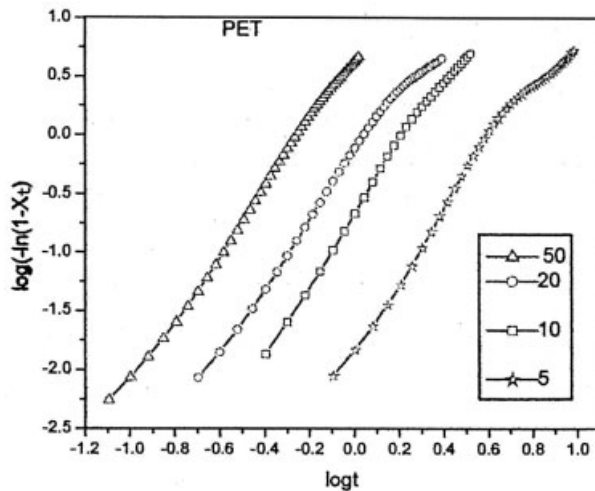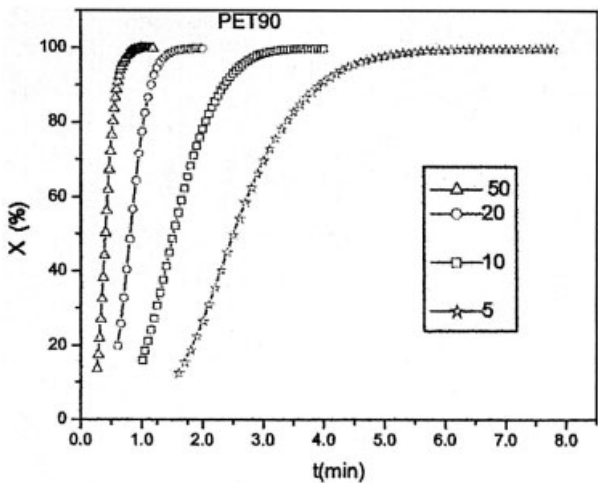
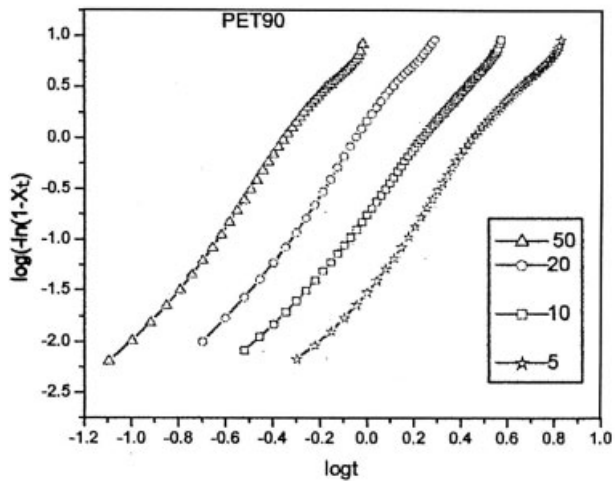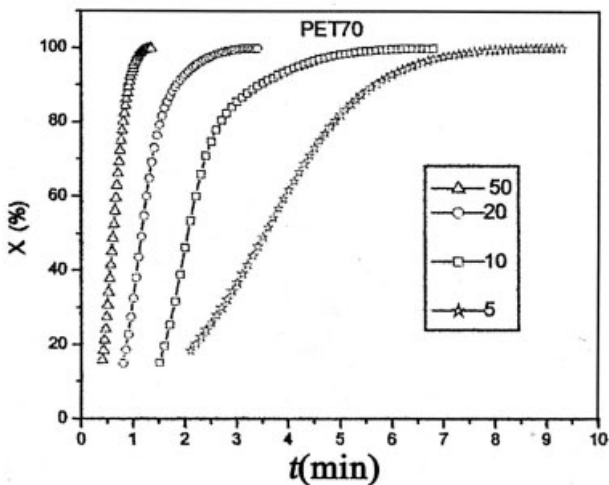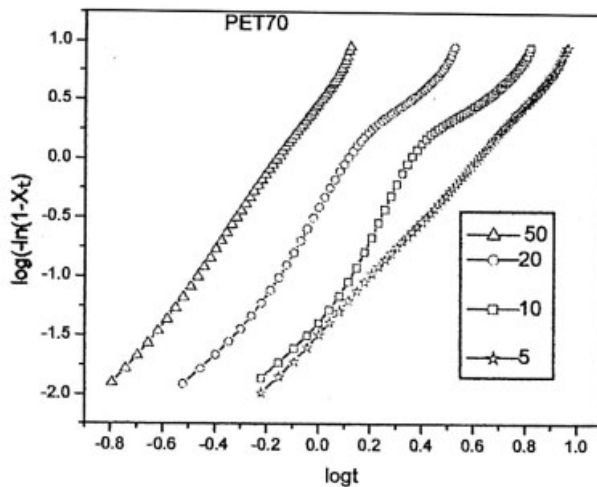**Figure 6** (a) Relation of crystallinity to time for pure PET. (b) for PET/phenoxy (90/10). (c) for PET/phenoxy (70/30) blends in non-isothermal crystallizaiton at different cooling rate.

Figure 7 (a) Relation of log[$-\ln(1-X_t)$] to log(t) for pure PET. (b) for PET/phenoxy (90/10). (c) for PET/phenoxy (70/30) blends in non-isothermal crystallization at different cooling rate.
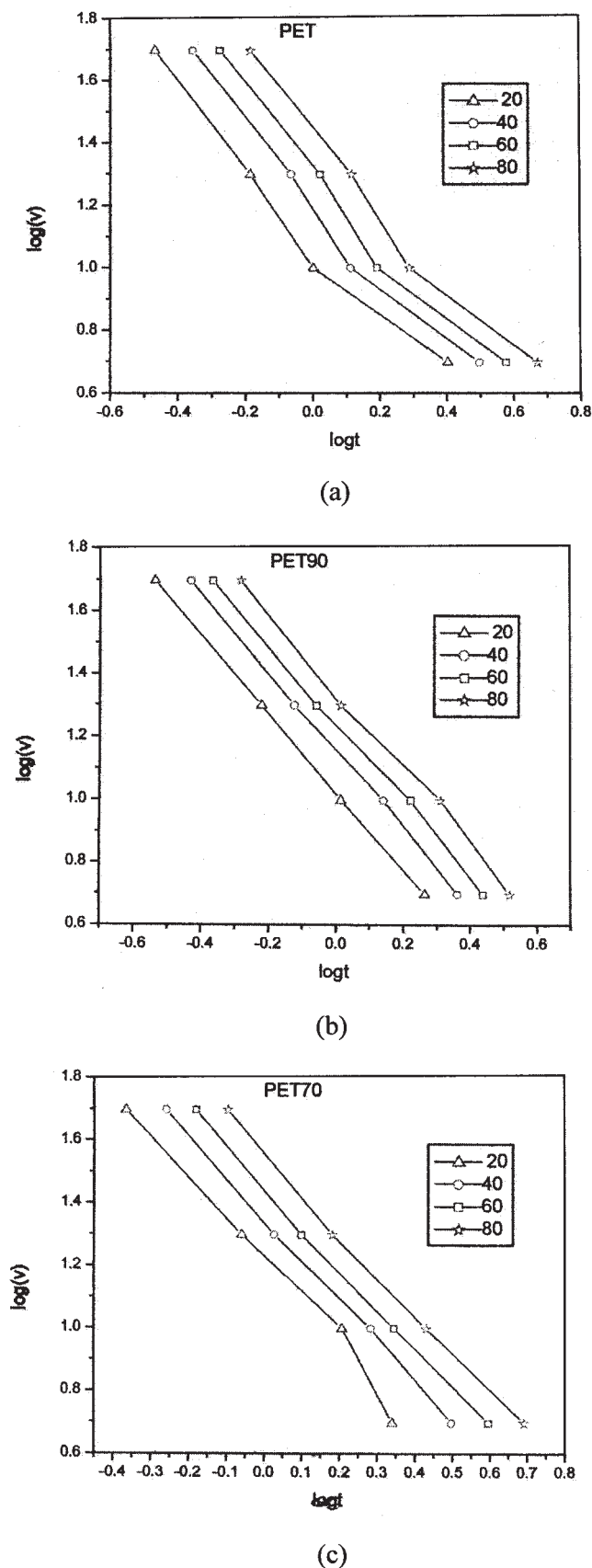
The results demonstrate that kinetic parameter $F(T)$ increases with increasing relative degree of crystallization, and the content of phenoxy, the composition of blend, and the relative degree of crystallization have almost no effect on the value of α.

CONCLUSIONS

Phenoxy has a substantial effect on PET crystallization because of the strong intermolecular interaction between PET and phenoxy. PET has an influence not only on the crystalline temperature of the PET blend but also on its crystalline perfection, which means that the crystalline structure becomes less perfect with increasing cooling crystallization temperature and decreasing crystallization temperature. The PET/phenoxy blend shows only one T_{g1}, the value of which is related to its heating history. When the PET content is not <30%, the glass transitions of samples are very similar to that of pure PET and basically do not change with blend composition. T_{g2}, obtained from the cooling curve, shows a positive deviation from the Fox equation, and T_{g3}, obtained in the secondary heating process, corresponds to the calculated value obtained by the Fox equation.

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(a)

(b)

(c)

Figure 8   (a) Relation of log(K) to log(t) for pure PET. (b) for PET/phenoxy (90/10). (c) for PET/phenoxy (70/30) blends in non-isothermal crystallization at different cooling rate.