Thermal and Crystallization Characteristics of Poly(ethylene terephthalate) with Poly(oxybenzoate-*p*-trimethylene terephthalate) Copolymer

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ABSTRACT: Poly(ethylene terephthalate) (PET) was blended with two different poly(oxybenzoate-*p*-trimethylene terephthalate) copolymers, designated T28 and T64, with the level of copolymer varying from 1 to 15 wt %. All samples were prepared by solution blending in a 60/40 (by weight) phenol/tetrachloroethane solvent at 50°C. The crystallization behavior of the samples was studied by DSC. The results indicate that both T28 and T64 accelerated the crystallization rate of PET in a manner similar to that of a nucleating agent. The acceleration of PET crystallization rate was most pronounced in the PET/T64 blends with a maximum level at 5 wt % of T64. The melting temperatures for the blends are comparable to that of pure PET. The observed changes in crystallization behavior are explained by the effect of the physical state of the copolyester during PET crystallization as well as the amount of copolymer in the blends. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1599–1606, 2002

Key words: blends; liquid–crystalline polymers; crystallization; differential scanning calorimetry (DSC); thermal properties

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a high-performance engineering plastic offering excellent thermal resistance, chemical resistance, and mechanical performance. Historically, it has not been considered for applications involving high-speed processing such as injection molding because it is a high melting and slow crystallizing polymer. However, crystallization can be increased by the addition of polymeric nucleating agents such as linear low-density polyethylene (LLDPE),[1] poly(methyl methacrylate) (PMMA),[2] poly(phenylene sulfide) (PPS),[3] high-density polyethylene (HDPE),[3] and liquid crystalline polymer (LCP).[4–7]

Blends of PET with a liquid crystalline polymer, LCP60–80 (blend of LCP60 and LCP80 in 50/50 wt %), at several compositions were studied by Baird et al.[5] They reported that the heat of fusion (ΔH_f) was seen to increase with increasing the LCP60–80 content. Other PET/LCP blends of PET/VLC (trade name Vectra A900) and PET/KLC (PHB/PET = 80/20 molar ratio) were studied by Misra et al.[7] VLC and KLC act like nucleating agents for PET crystallization, and this ef-

fect probably reaches a maximum at an LCP level between 0 and 5 wt %. In the range from 10 to 15 wt %, VLC and KLC possibly destroy the symmetry of PET, thus resulting in the decreases in ΔH_f, heat of crystallization (ΔH_c), and endothermic melting peak (T_m). From these earlier results, it is seen that the crystallization behavior of PET blends is influenced by the composition and amount of the second component, chemical compatibility, and the degree of dispersion achieved in the mixing process. Poly(trimethylene terephthalate) (PTT) is one member of the terephthalic polyesters, which are common substances used in engineering thermoplastics. In recent years, PTTs have drawn attention for applications in the textile industry because of a great reduction in the manufacturing cost of 1,3-propanediol, the monomer used for PTT synthesis.[8]

In this work, the melting and crystallization behavior of a commercial PET resin blended with two different poly(oxybenzoate-*p*-trimethylene terephthalate) copolyesters (POB/PTT) were studied by the aid of DSC. The objective of this investigation was to elucidate the effects of composition and amount of the copolyester component on the PET crystallization rate.

EXPERIMENTAL

Materials

POB/PTT copolyesters, designated T28 and T64, were synthesized following the method presented by Kuh-

fuss and Jackson.[9] These copolyesters contain different POB/PTT molar ratios: 20/80 in T28 and 60/40 in T64. PET was a commercial product from the Far East Textile Co. (Taoyuan, Taiwan). The inherent viscosities of T28 and T64 were 0.56 and 0.89 dL/g, respectively, measured at 30°C in 60/40 (by weight) phenol/tetrachloroethane at a concentration 0.50 g/100 mL. The intrinsic viscosity of PET was 0.62 dL/g when it was measured at 30°C with the same mixed solvent as T28 and T64. The crystallization and melting characteristics of T28 and T64 were as follows: there is a distinct exothermic crystallization peak in the cooling scans for T28 (T_c = 173°C). There is no distinct crystallization peak for T64. In the heating scans, there is a distinct endothermic melting peak for T28 (T_m = 214°C). T64 showed broad and obscurely small melting peaks at 160 and 180°C. PET and the copolyesters were dried *in vacuo* at 70°C for 48 h before solution blending.

Blending method

Two sets of blends were prepared, one with T28, designated as PET/T28; and the other with T64, designated as PET/T64. Four compositions were prepared with PET/T28 and PET/T64 weight ratios of 99/1, 95/5, 90/10, and 85/15. The solution blends of the different compositions used were prepared by dissolving an amount of PET/copolyester in the desired weight ratio in 60/40 (by weight) phenol/tetrachloroethane solvent at 50°C. The total concentration was in the vicinity of 10% in weight. These solutions were stirred for 3 h and then were added dropwise to a large excess of cold methanol at 0°C, causing rapid coprecipitation. The precipitate was filtered off and washed with methanol to remove the phenol/tetrachloroethane solvent completely. The final precipitate was dried completely *in vacuo* at 70°C. The pure PET was also subjected to identical processing in the phenol/tetrachloroethane solvent to nullify the effects of thermal history.

DSC measurement

The weight of all samples was kept between 10 and 11 mg for DSC. DSC measurements were performed with TA 2010 analyzer (TA Instruments, New Castle, DE). The samples were maintained at 280°C for 3 min in nitrogen atmosphere to destroy anisotropy. Subsequently, the samples were cooled at 10°C/min to 30°C and then again heated at 10°C/min to 280°C to obtain cooling and heating curves, respectively. Both crystallization and melting parameters were obtained from the cooling and heating scans. T_m was considered to be the maximum of the endothermic melting peak from the heating scans and T_c that of the exothermic peak of the crystallization from the cooling scans. Melting

heats (ΔH_f) and crystallization heats (ΔH_c) were determined from the areas of melting peaks and crystallization peaks, respectively. The ΔH_c and ΔH_f refer to the whole blends. All results are the average of three samples.

Polarized light microscopy (PLM)

The microscopic observations were performed with a polarized light microscope (Olympus BX51-P; Olympus, Melville, NY). The specimens, held between two thin microscope coverslips, were prepared on the hot stage preheated to 280°C. The blends were melted, followed by pressure on the upper coverslip, and then quenched by liquid nitrogen. The photomicrographs were obtained at room temperature.

RESULTS AND DISCUSSION

Composition effect by blending different weight percentages of T28 copolyester

Figure 1 shows cooling and heating curves for PET/T28 blends. The various parameters determined from these curves are given in Table I. It is evident that there is a distinct exothermic crystallization peak in all of the cooling scans and there is an endothermic melting peak in all of the heating scans.

The crystallization onset temperatures and crystallization temperatures (T_c) for PET/T28 blends are higher than that of pure PET in all four compositions. The 95/5 PET/T28 blend exhibits the highest crystallization onset temperatures and T_c among the PET/T28 blend system. Changes in the crystallization peak width (ΔT_c) and the heat of crystallization (ΔH_c) are related to the overall crystallization rate and the extent of crystallization, respectively. The ΔT_c's for the blends are narrower by 17 to 19°C than that of pure PET (57°C) and the 95/5 PET/T28 blend exhibits the narrowest ΔT_c. On the other hand, values of ΔH_c for blends are greater than that of PET (34.1 J/g), except for the 99/1 PET/T28 blend. If the crystallization rate were defined as the heat of crystallization divided by the time from the onset to completion of crystallization (ΔH_c/time), then the crystallization rates for the PET/T28 blends are always greater than that of PET (0.100 J g^{-1} s^{-1}), as seen in Table I, and the 95/5 blend exhibits the greatest value of ΔH_c/time (0.168 J g^{-1} s^{-1}). In other words, 5 wt % T28 accelerates PET crystallization rate 1.68 times. In programmed cooling, the crystallization temperature reflects the overall crystallization rate attributed to the combined effects of nucleation and growth. Thus the degree of supercooling ($\Delta T = T_m - T_c$) may be a measurement of a polymer's crystallizability; that is, the smaller the ΔT, the higher the overall crystallization rate. The ΔT values for the PET/T28 blends are smaller, by 13 to 18°C,
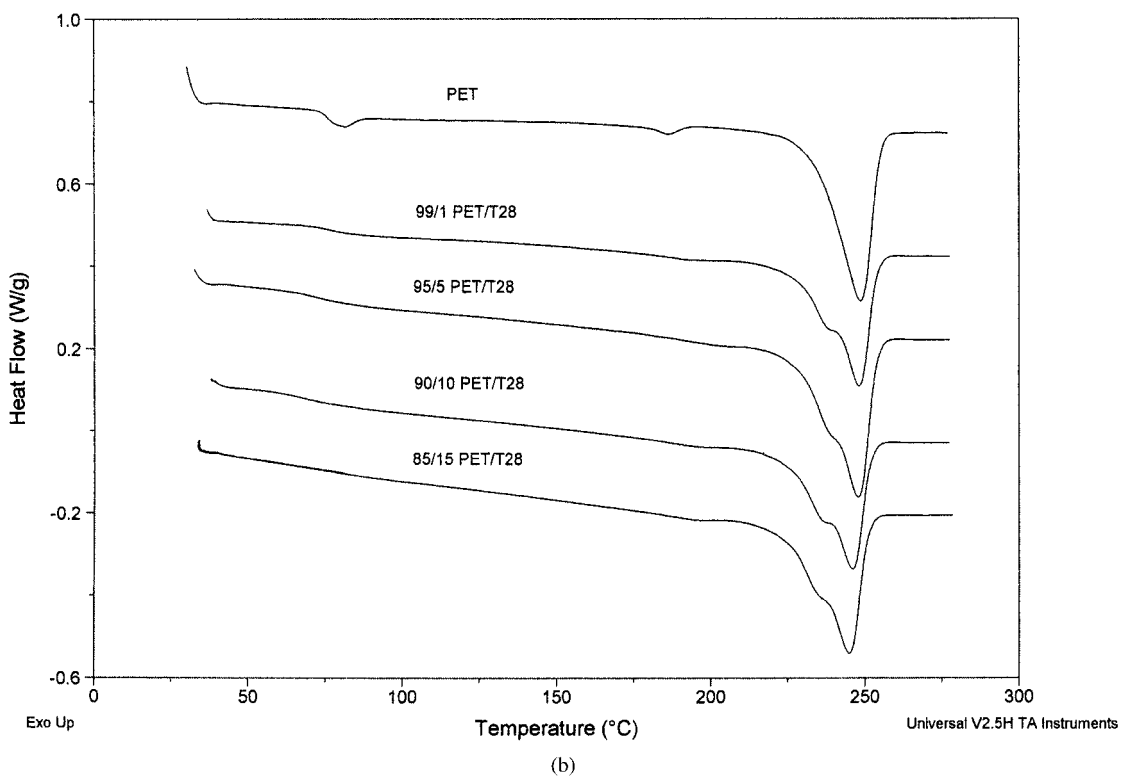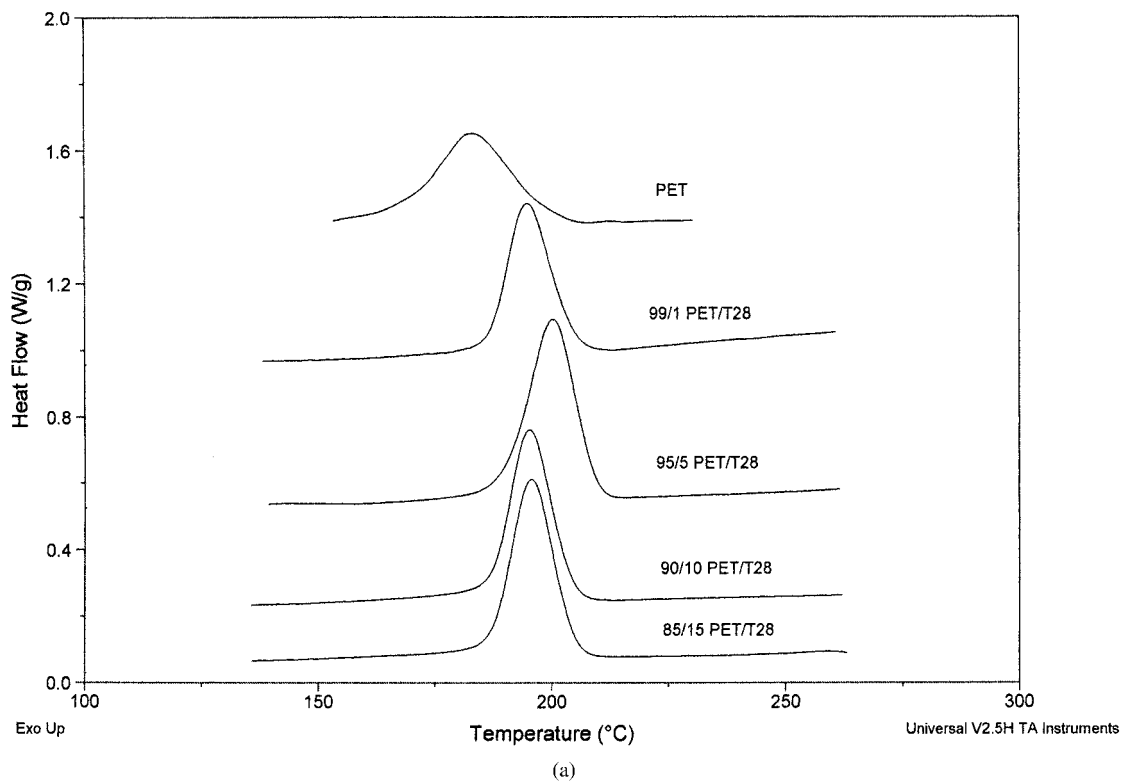
(a)

(b)

Figure 1 DSC thermograms of PET and PET blends with 1–15 wt % of T28 copolyesters: (a) heating scans; (b) cooling scans.

than that of pure PET (66°C). The result again reveals that the overall crystallization rate for the PET/T28 blends is greater than that of PET. As shown in Table I, the 95/5 PET/T28 blend exhibits the highest crystallization onset temperature and T_c. On the other hand, the 95/5 PET/T28 blend exhibits the greatest ΔH_c (40.4 J/g) and ΔH_c/time (0.168 J g^{-1} s^{-1}), and the smallest ΔT (48°C) among the PET/T28 blends. These

TABLE I
DSC Data of PET Blends with Different Weight Percentages of T28 and T64

| Composition | Melting (from heating scans) | | | | Crystallization (from cooling scans) | | | | | |
	Onset (°C)	T_m (°C)	ΔT_m (°C)	ΔH_f (J/g)	Onset (°C)	T_c (°C)	ΔT_c (°C)	ΔH_c (J/g)	ΔH_c/time (J g^{-1} s^{-1})	ΔT^a (°C)
PET/T28										
100/0	200	249	62	35.4	211	183	57	34.1	0.100	66
99/1	212	248	49	28.9	213	195	38	31.7	0.139	53
95/5	210	248	50	35.9	215	200	40	40.4	0.168	48
90/10	207	246	50	30.0	212	195	38	34.4	0.151	51
85/15	207	245	51	32.2	212	196	39	34.8	0.149	49
PET/T64										
99/1	210	249	53	36.5	216	200	33	38.2	0.193	49
95/5	211	248	51	40.1	214	201	30	43.6	0.242	47
90/10	210	247	50	35.0	210	197	26	36.0	0.231	50
85/15	209	245	50	30.9	210	197	25	34.3	0.229	48

^{a} $\Delta T = T_m - T_c$.

results imply that the crystallization of PET may be accelerated by means of blending with 1–15 wt % T28 copolyester, and the acceleration effect probably reaches a maximum at a T28 level of 5 wt %.

The various melting parameters determined from heating scans for PET/T28 blends are summarized in Table I. The melting temperatures (T_m) of all blends remain about the same as that of PET (249°C), except for the 85/15 blend (245°C). The onset temperature of melting and melting peak width (ΔT_m) are related to the least stability and distribution of crystallites, respectively. A clear increase (7–12°C) of the onset temperature of melting is found in the blends with respect to that of pure PET (200°C). A clear decrease (11–13°C) in ΔT_m is found in the blends with respect to that of pure PET (62°C). These results indicate that the PET crystallites in the PET/T28 blends with 1–15 wt % of T28 copolyester are more perfect than those found in pure PET.

## Composition effect by blending different weight percentages of T64 copolyester

Figure 2 shows cooling and heating curves for PET/T64 blends. The various parameters determined from these curves are given in Table I. It is evident that there is a distinct exothermic crystallization peak in all of the cooling scans and there is an endothermic melting peak in all of the heating scans.

In the PET/T64 blends, the T_c values are higher by 14–18°C than that of pure PET in all four compositions. The 95/5 PET/T64 blend exhibits the highest T_c. The values of ΔH_c for T28 and T64 are 44.6 and 0.0 (J/g), respectively. The computed value of ΔH_c, by using the rule of additivity and after normalizing for their respective weight fractions, varies with the blend composition, as shown in Figure 3, where computed and experimental results are compared for the PET/T64 blends. These blends exhibit higher experimental

ΔH_c values than those computed over the level of 1–15 wt % of T64, indicating that PET is crystallized to a greater extent than expected, by blending with T64 at the level of 1–15 wt %. The values of ΔH_c/time for the blends are always greater than that of PET (0.100 J g^{-1} s^{-1}) and the 95/5 blend exhibits the greatest value of ΔH_c/time (0.242 J g^{-1} s^{-1}). In other words, 5 wt % T64 accelerates PET crystallization rate 2.42 times. The ΔT for the blends are smaller by 16 to 19°C than that of pure PET (66°C) and the 95/5 blend exhibits the smallest value of ΔT. These results imply that the crystallization rate of PET may be accelerated by means of blending with 1–15 wt % T64. The acceleration of PET crystallization is most pronounced in the 95/5 blend, because it exhibits the highest T_c (201°C), the greatest ΔH_c (43.6 J/g) and ΔH_c/time (0.242 J g^{-1} s^{-1}), and the smallest ΔT (47°C) among PET/T64 blends.

The various melting parameters of the PET/T64 blends, determined from heating scans, are summarized in Table I. The T_m's of all blends remain about the same as that of PET (249°C), except for the 85/15 blend (245°C). A clear increase (9–11°C) of the onset temperature of melting is found in the blends with respect to that of pure PET (200°C). A clear decrease (9–12°C) in ΔT_m is found in the blends with respect to that of pure PET (62°C). These results indicate that the PET crystallites in the PET/T64 blends with 1–15 wt % of T64 copolyester are more perfect than those found in pure PET.

A comparison of the crystallization parameters of two blend systems with the same content of copolyester (shown in Table I) shows that the values of T_c of PET/T64 blend are higher than those of the PET/T28 blends. The value of ΔT_c of PET/T64 blend is narrower than that of PET/T28 blend. The values of ΔH_c/time of PET/T64 blend are significantly greater than those of PET/T28 blend. The values of ΔT of PET/T64 blend are smaller than those of PET/T28
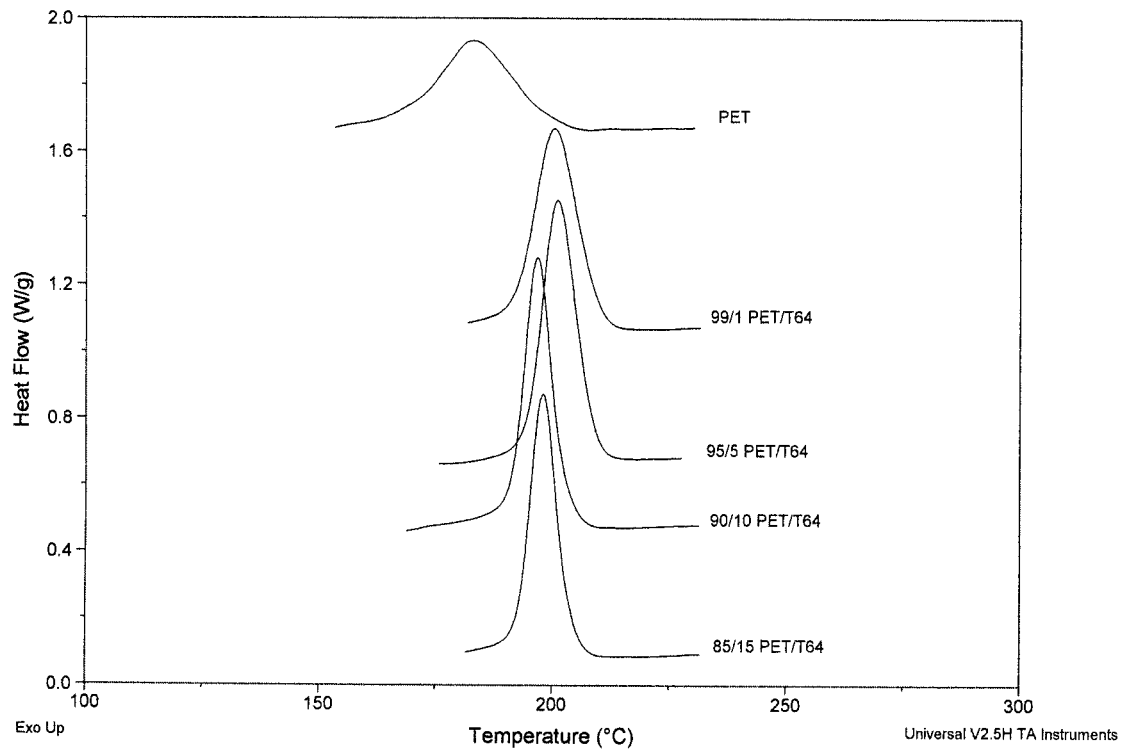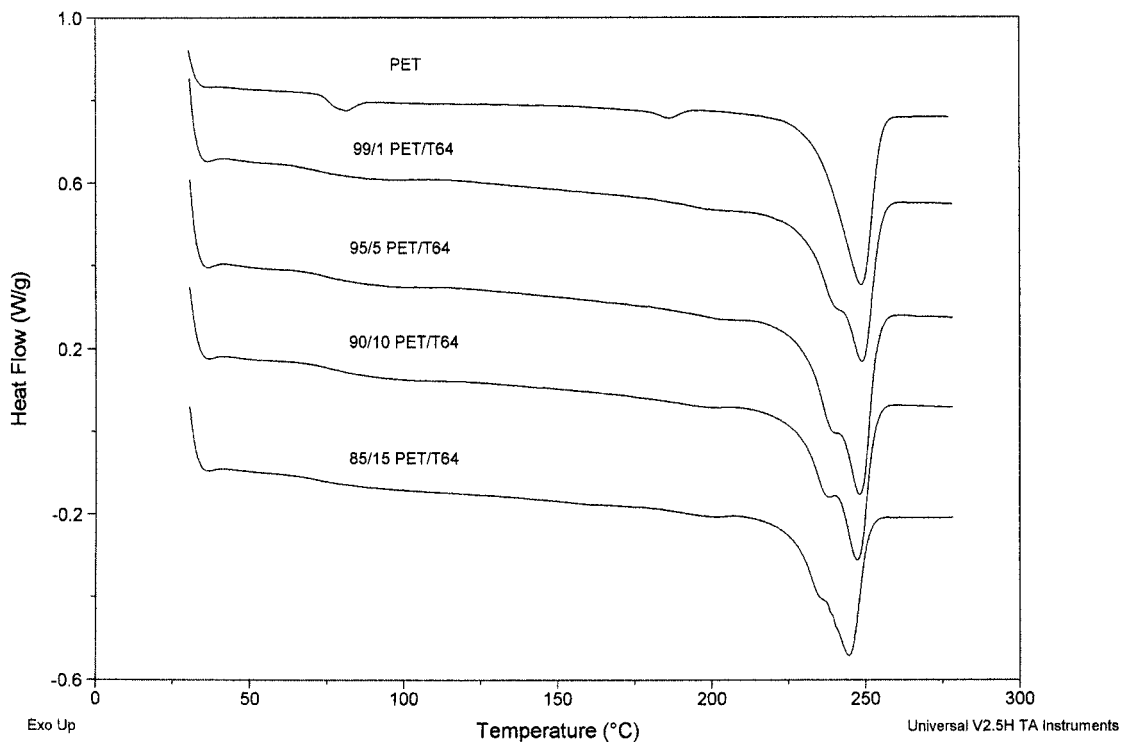
Figure 2 DSC thermograms of PET and PET blends with 1–15 wt % of T64 copolyesters: (a) heating scans; (b) cooling scans.

blend. The higher the value of T_c, the higher the crystallization rate. The greater the value of ΔH_c/time, the higher the crystallization rate. The smaller the value of ΔT, the higher the crystallization rate. These results reveal that crystallization of PET is accelerated more significantly by T64 than by T28 with the same wt % of copolyester. As can be seen in Figure 4, the crystallization rates (ΔH_c/time) for the PET/T28 and PET/T64
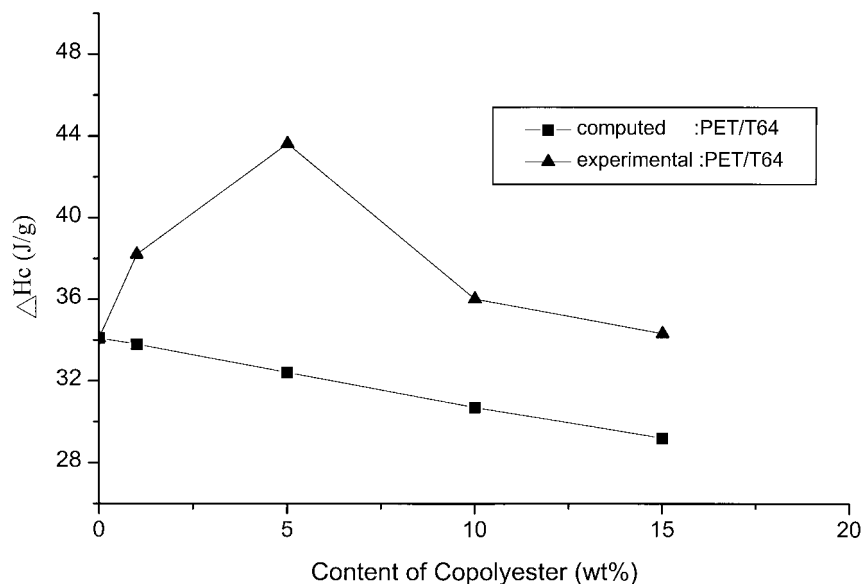
Figure 3 Composition dependency of heat of crystallization of PET in the PET/T64 blends.

blends are always greater than that of pure PET and the crystallization rate of PET/T64 blend is always greater than that of PET/T28 blend with the same wt % of copolyester. The result again reveals that the crystallization rate of PET is accelerated more significantly by T64 than by T28. In both blend systems, 95/5 PET/T64 blend exhibits the most significant acceleration of PET crystallization rate because of the highest T_c (201°C), the smallest ΔT (47°C), and the greatest ΔH_c (43.6 J/g) and ΔH_c/time (0.242 J g^{-1} s^{-1}) among the PET/T28 and PET/T64 blend systems.

In general, where units of the same chemical structure in two distinct polymers cocrystallize, adjacent and dissimilar units of polymer components in the polyblends can act as impurities and deform the crystal structure.[10] Thus, depressions of the values of T_m and ΔH_f with blend composition are often observed. The retardation of PET crystallization and lowering of its degree of crystallinity and crystallization rate in miscible blends of PET/PAr (polyarylate of bisphenol A and 50/50 isophthalic/terephthalic acids) have been reported.[11–15] The decrease in the crystallinity of these blends was attributed to the inclusion of the rigid PAr unit in PET chains, which causes a decrease in their crystallizable segment length. Our previous study,[16] which investigated the effect of the transesterification
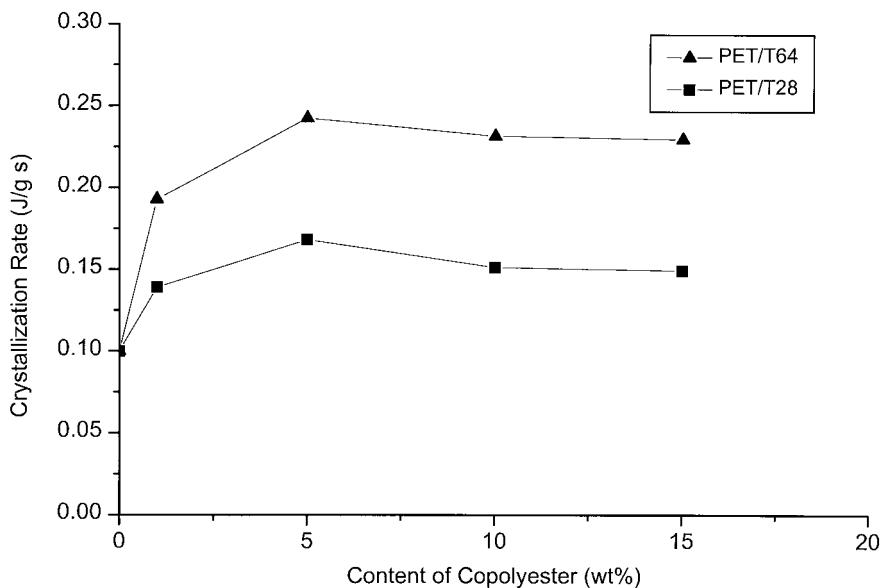

Figure 4 Crystallization rate of PET blends with 1–15 wt % of T28 and T64 copolyesters. The point at 0 wt % corresponds to pure PET.

in the 50/50 PET/P46 blend after different times, reveals that the crystallization rate decreased with increasing melting blending time [P46 is a copolyester of a PET modified by 40 mol % p-oxybenzoate (POB)].

These results may be attributed to a hindered crystallization that transesterification would induce because of POB unit inclusion in the PET crystal as a defect and to the concomitant decrease in the crystallized segment length of PET. In this research, because the absence of transesterification was confirmed by nuclear magnetic resonance measurement on the blend before and after solution blending, the effect of transesterification on the crystallization rate of PET blends does not need to be considered. The crystallization rate of PET was accelerated by blending with the T28 and T64 copolyesters over the content range from 1 to 15%, and the 95/5 PET/T64 blend exhibits the most significant acceleration of PET crystallization rate. This may be explained as follows: (1) The T_c of T28 is 173°C, and no crystallization peak was detected for T64, respectively. In the blend, PET crystallizes in the presence of these second component melts. The melts of these copolyesters, which exhibit a high degree of molecular order of the anisotropic phase, even the liquid crystalline T64, accelerate the nucleation and growth process in a manner similar to that of a nucleating agent. (2) From the results of our previous study,[17] the distribution of PET crystallites and the crystallization behavior are a function of the POB content in the blend of PET with PET–POB copolyesters. In this research, the 95/5 PET/T64 blend exhibits perhaps a proper extent of molecular order of the anisotropic phase and a proper POB content that may not destroy the symmetry of PET, thus resulting in a significant acceleration in PET crystallization rate. The hindering effect on crystallization resulting from the transesterification during the cooling scan may be neglected because of the lesser content of POB. Thus, the 95/5 PET/T64 blend most significantly accelerates crystallization among the PET/T28 and PET/T64 blend systems.

Polarized light microscopy

Figure 5 shows polarized optical micrographs of PET with different weight percentages of T28 and T64. The optical micrographs of the PET/T28 blend are presented in Figure 5(a)–(c). We find that the crystalline texture consists of isotropic and anisotropic phases, which can be characterized as a liquid crystalline region of POB rich in bright or brown color based on the high birefringence under cross polarizers. The anisotropic phase is scattered in the isotropic matrix phase and increases with the content of T28 in the blend. For PET/T28 blends with T28 under 5 wt %, the anisotropic phase is fine and dispersed in the PET matrix. In the 90/10 PET/T28 blend, there are large aggregates
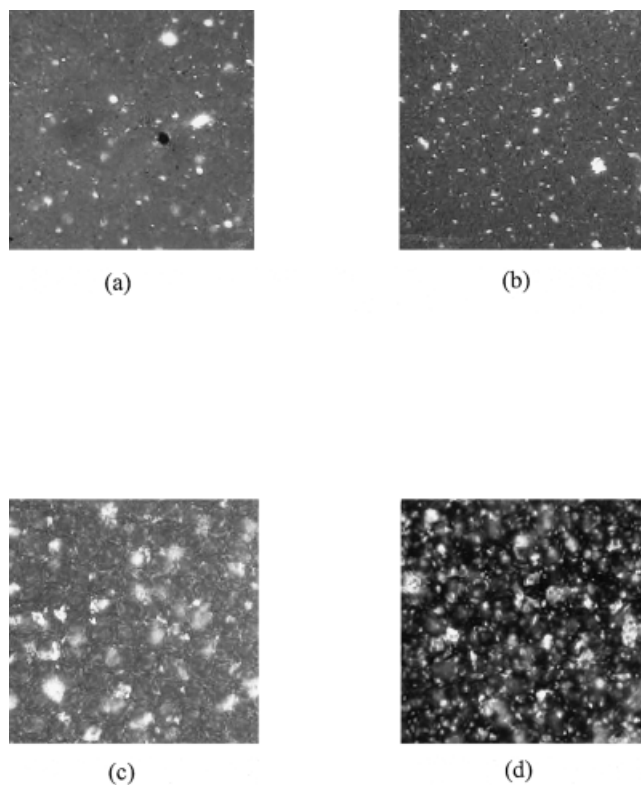

Figure 5 Polarized light micrographs of samples: (a) 99/1 PET/T28 blend; (b) 95/5 PET/T28 blend; (c) 90/10 PET/T28 blend; (d) 95/5 PET/T64 blend (×375).

of T28 copolyester because of the higher content of T28. T64 is a liquid crystalline polymer but T28 exhibits a partly anisotropic phase. The fact that there are more large aggregates and bright spots in 95/5 PET/T64 [Fig. 5(d)] than in the 95/5 PET/T28 [Fig. 5(b)] is reasonable. The good distribution of the nucleating agent is responsible for the crystallization rate of the matrix because of the uniformity of the nucleating spots of crystallization. The morphologic observations of PLM confirm again that the T28 and T64 were highly efficient nucleating agents for PET at 1–15 wt %.

CONCLUSIONS

It is known that the crystallization behavior of a polymer becomes modified in a blend because of the presence of the other component. The results of the present investigation clearly indicate that this modification depends on composition and the amount of the second component. It was found that T64 copolyester accelerates the crystallization rate of PET more significantly than did the T28 copolyester, when it is blended into PET at a level of 1–15 wt %. The 95/5 PET/T64 blend exhibits the most significant acceleration of PET crystallization over the copolyester content

range from 1 to 15 wt % for PET/T28 and PET/T64 solution blends.

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