

Blends of Poly(ethylene terephthalate) with Co[poly(ethylene terephthalate-*p*-oxybenzoate)].

II. Composition Effect on the Rate of Crystallization

CHENG-FANG OU and CHEN-CHONG LIN*

Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan, Republic of China

SYNOPSIS

Poly(ethylene terephthalate) (PET) was blended with four different kinds of co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters, designated P28, P46, P64, and P82, with the level of copolyester varying from 1 to 15 wt %. All samples were prepared by melt-mixing in a Brabender Plasticorder for 8 min. The crystallization behavior of samples were then studied via DSC. The results indicate that these four copolyesters accelerate the crystallization rate of PET in a manner similar to that of a nucleating agent. The acceleration of the PET crystallization rate was most pronounced in the PET/P28 blends with a maximum level at 10 wt % of P28, and in the PET/P82 blends, at 5 wt % of P82. The melting endotherm onset temperatures and the melting peak widths for the blends are comparable with those of neat PET. These results imply that the stability of PET crystalline phase in the blends does not change by blending. The observed changes in crystallization behavior, however, are explained by the effect of the physical state of the copolyester during PET crystallization as well as the content of the *p*-oxybenzoate (POB) moiety incorporated into the blends. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a versatile polymer used in synthetic fiber, blow-molded containers, and packaging film. Historically, it has not been considered for applications involving high-speed processing such as injection molding because it crystallizes very slowly from the melts. 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

An earlier nonisothermal crystallization study showed that PET crystallization from the melt facilitated by the presence of solidified PPS in PET/PPS blends, as shown by an increase of the crystallization onset temperature by 6–10°C and also by

a narrowing of of the crystallization exotherm peak width (ΔT_c).³ The alloying of PET with PMMA was reported to accelerate the crystallization significantly and was most pronounced in an 85/15 PET/PMMA blend.² 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 effect probably reaches a maximum at a 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 , ΔH_c , and 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.

* To whom correspondence should be addressed.

Table I Melting and Crystallization Parameters of Polymers Used for Blending (from DSC Scans)

Composition	Melting (Heating Scan)			Crystallization (Cooling Scan)			
	T_g (°C)	T_m (°C)	ΔH_f (J/g)	Onset (°C)	T_c (°C)	ΔT_c (°C)	ΔH_c (J/g)
PET	73	253	39.7	216	200	37	39.9
P28	74	210	32.3	183	168	37	32.1
P46	82	191	13.2	187	172	37	8.3
P64	75	158	4.7	159	138	48	2.7
P82	72	—	—	—	—	—	— ^a

^a Cannot be detected.

In this study, we report the crystallization and melting behavior of a commercial PET resin blended with four types of co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters (POB-PET). POB-PET copolyesters with a POB unit content from 40 to 90 mol % are well-known thermotropic copolyesters developed by Tennessee Eastman Co.⁸⁻¹⁰ 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

Four co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters, designated as P28, P46, P64, and P82, were synthesized according to the procedure reported in our previous study.¹¹ These copolyesters contain different POB/PET mol ratios: 20/80 in P28, 40/60 in P46, 60/40 in P64, and 80/20 in P82. PET was a commercial product from the Far East Textile Co. (Taiwan) having an intrinsic viscosity (I.V.) of 0.62 (dL/g) measured at 30°C in 60/40 phenol/tetrachloroethane (by weight). PET and the nucleating copolyesters were dried at 70°C for 48 h in a vacuum oven prior to blending.

Blending Method

The blends were prepared by melt-compounding on a Brabender Plasticorder with a batch-type roller mixer in various PET/copolyester weight ratios. The compounding was done at a temperature of 300°C for 8 min and at a rotor speed of 30 rpm. After blending, the sample was taken from the bowl and immediately quenched in liquid nitrogen. Four com-

positions were prepared with PET/P28 and PET/P82 weight ratios of 99/1, 95/5, 90/10, and 85/15. The PET/P46 and PET/P64 were made only at a 90/10 composition. The neat PET was also subjected to identical processing in the Brabender mixer in order to nullify the effects of thermal history.

DSC Measurement

Blend samples were reduced to about 0.5 mm in diameter by a cutting mill. The weight of all samples was kept between 10 and 11 milligrams for DSC evaluation using a Seiko SSC-5200.

Samples were heated to 305°C at a heating rate of 10°C/min under a nitrogen atmosphere, held for 5 min to destroy anisotropy, and then cooled down at 10°C/min to 20°C. Both melting and crystallization parameters were obtained from the heating and cooling scans.

RESULTS AND DISCUSSION

The various melting and crystallization parameters determined from heating and cooling scans of the neat polymers used for blending in this study are shown in Table I. The normal temperature range for crystallization of PET from melt is between 179 and 216°C. The ranges of crystallization temperatures of P28, P46, and P64 are narrower than that of PET. A transition from solid to liquid crystalline states at about 299°C was observed from the heating scan of P82. Thus, in the PET/P82 blend, PET crystallizes in the presence of solidified P82, whereas in the blends with P28, P46, and P64, the PET crystallizes in the presence of the melts of these second components.

Both a recrystallization exothermic peak and a

melting endothermic peak were in all the heating scans, and there was only a distinct crystallization exothermic peak in all the cooling scans for PET blends with 10% POB-PET copolyester as reported in our previous article.¹² The DSC data from the heating scans for all samples with 10 wt % copolyesters are tabulated in Table II(a). The blends exhibit the depressions of recrystallization onset temperature and recrystallization temperature (T_{rc}) by recrystallization and increase in the heat of fusion (ΔH_f) by melting if compared with those of PET. This indicates that the degree of crystallinity of PET increases upon addition of the copolyesters. It is known that the total crystallinity (ΔH_f) of a resin is the sum of primary crystallinity and secondary crystallinity. Although the extent of primary crystallinity cannot be directly monitored at a rapid cooling rate, it can be estimated, from the heating curve, as the difference between the area under the induced secondary crystallinity peak (ΔH_{rc}) and the area of the total crystallinity melting peak (ΔH_f). It is seen that the primary crystallinities (i.e., $\Delta H_f - \Delta H_{rc}$) are increased in all the blends. This indicates that the primary crystallization of PET is accelerated in the presence of 10 wt % copolyester after

blending. The melting temperatures of all blends are the same as that of PET (253°C). Temperature at the onset of melting and melting peak width (ΔT_m) are related to the least stability and distribution of crystallites, respectively. These parameters are found to be comparable with those of neat PET. This suggests that the least stability and distribution of PET crystallites in the blends is not significantly influenced by blending with 10 wt % copolyesters.

The crystallization parameters of blends obtained from the cooling scans are given in Table II(b). A shift in the crystallization onset temperature represents modification of the nucleation process. Changes in the crystallization peak width and the heat of crystallization (ΔH_c) are related to the overall crystallization rate and the extent of crystallization, respectively. The crystallization onset temperatures of the blends are higher by 1–6°C than that of the PET (216°C), except for the PET/P46 blend. The crystallization peak temperature (T_c) represents the temperature at maximum crystallization rate. Also, these temperatures for the blends are higher by 2–11°C than that of neat PET (200°C). The crystallization onset temperature and crystallization peak temperature for the PET/P28 blend are the highest

Table II DSC Data of PET and PET Blends with 10 Wt % Different Copolyesters

(a) From Heating Scans										
Composition (90/10)	T_g (°C)	Recrystallization				Melting			Difference	
		Onset (°C)	T_{rc} (°C)	ΔT_{rc} (°C)	ΔH_{rc} (J/g)	Onset (°C)	T_m (°C)	ΔT_m (°C)	ΔH_f (J/g)	$\Delta H_f - \Delta H_{rc}$ (J/g)
PET	73	116	133	34	26.9	220	253	47	39.7	12.8
PET/P28	76	109	127	34	23.8	219	253	48	47.0	23.2
PET/P46	78	110	127	33	16.8	219	253	49	43.3	26.5
PET/P64	77	110	125	30	11.5	222	253	46	40.5	29.0
PET/P82	74	111	129	36	20.4	219	253	48	40.7	20.3

(b) From Cooling Scans						
Composition (90/10)	Crystallization				ΔH_c (J/g)	Content of POB (Wt %)
	Onset (°C)	T_c (°C)	ΔT_c (°C)			
PET	216	200	37		39.9	0.00
PET/P28	222	211	30		44.8	1.35
PET/P46	216	202	32		42.0	2.94
PET/P64	217	203	35		41.4	4.83
PET/P82	218	205	33		41.3	7.12

among all blends. All the crystallization exotherm widths are narrower, and heats of crystallization are greater for the blends if compared to neat PET. The PET/P28 blend exhibits the narrowest crystallization width (30°C) and the greatest heat of crystallization (44.8 J/g) among all blends. These results imply that the crystallization of PET can be accelerated by blending with 10 wt % copolyesters: e.g., P28, P46, P64, and P82. Furthermore, the acceleration of PET crystallization is most pronounced in the PET/P28 blend.

The retardation of PET crystallization and lowering of its degree of crystallinity and crystallization rate in miscible blends with polycarbonate and polyarylates have been reported by Eguiazabal et al.¹³⁻¹⁷ The decrease in the crystallinity of these blends was attributed to chemical interaction. It is important to note that P28, P46, P64, and P82 are a series of copolyesters of PET, and, hence, a certain degree of compatibility caused by transesterification must be taken into consideration, especially in the PET blending process. The transesterification reaction would induce POB unit inclusion in the PET crystal as a defect, resulting in the retardation of the PET crystallization rate. The effect of POB content in the blends on the crystallization behavior is shown in Figure 1. The blend with POB content of 1–2 wt % exhibits the narrowest crystallization width and the greatest heat of crystallization. The 90/10 PET/P28 blend with 1.35 wt % POB exhibits the most pronounced acceleration of PET crystallization [see Table II(b)]. This is perhaps the result of minimal transesterification, providing the most effective nucleation and accelerated crystal growth. Although in the PET/P46 and PET/P64 blends PET would crystallize by homogeneous nucleation similarly to the PET/P28 blend, the extent of transesterification may be greater than that of the PET/P28 blend owing to a greater POB content in the PET/P46 (2.94 wt %) and PET/P64 (4.83 wt %) blends. Thus, the acceleration of PET crystallization in these two blends was not as significant as it was in the PET/P28 blend.

To confirm the composition dependence of the crystallization of PET in the blends, the PET/P28 and PET/P82 blends were subjected to further studies. Four compositions were prepared in weight ratios of 99/1, 95/5, 90/10, and 85/15. The melting parameters determined from heating scans are summarized in Table III(a). It is obvious that onset temperatures of recrystallization and recrystallization temperatures are lower than those of neat PET, and the values of primary crystallinity (i.e., $\Delta H_f - \Delta H_{rc}$) are higher than that of neat PET for these blends

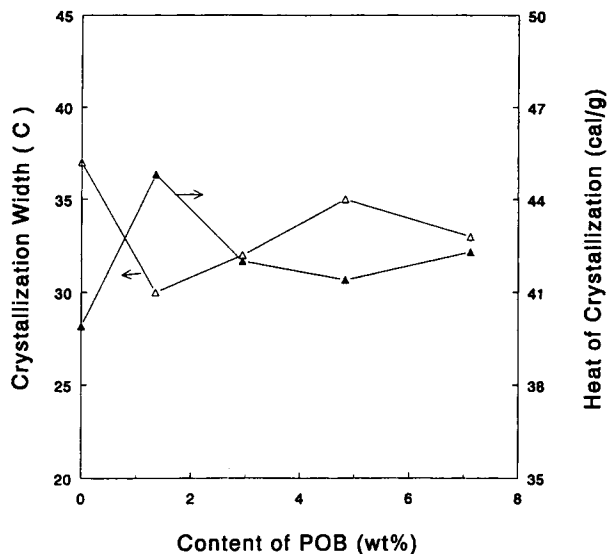


Figure 1 Variation of the crystallization width and heat of crystallization of PET with POB content in the PET/P28, PET/P46, PET/P64, and PET/P82 blends at a 90/10 composition.

of four compositions. Onset temperatures of melting and melting peak widths are comparable with those of neat PET. This indicates that the primary crystallization of PET is accelerated by blending with 1, 5, 10, and 15 wt % of P28 or P82 copolyester, whereas the least stability and distribution of PET crystallites does not significantly change.

The composition dependence of the crystallization parameters during cooling of the PET/P28 and PET/P82 blends are given in Table III(b). The crystallization onset temperatures and crystallization peak temperatures for PET/P28 and PET/P82 blends are higher than those of neat PET in all four compositions. The crystallization widths are narrower than that of neat PET (37°C) in all but the 99/1 PET/P28 blend. The crystallization width is decreased with an increasing amount of copolyester in the PET/P28 blends, but it remains almost the same in PET/P82 blends. The heats of crystallization for the PET/P28 and PET/P82 blends are always greater than that of neat PET. The computed value of the heat of crystallization by using the rule of additivity and after normalizing for their respective weight fractions varies with the blend composition as shown in Figure 2, where computed (unbroken line) and experimental (dashed line) results are compared for the PET/P28 and PET/P82 blends. These blends exhibit higher experimental heats of crystallization than those computed over the entire composition range, indicating that PET is crystallized to a greater extent than expected, by

Table III DSC Data of PET Blends with Different Wt % of P28 and P82

(a) From Heating Scans										
Composition	T_g (°C)	Recrystallization				Melting				Difference
		Onset (°C)	T_{rc} (°C)	ΔT_{rc} (°C)	ΔH_{rc} (J/g)	Onset (°C)	T_m (°C)	ΔT_m (°C)	ΔH_f (J/g)	$\Delta H_f - \Delta H_{rc}$ (J/g)
PET/P28										
100/0	73	116	133	34	26.9	220	253	47	39.7	12.8
99/1	74	113	130	29	22.7	220	253	48	42.0	19.3
95/5	73	110	130	30	24.7	220	253	48	46.3	21.6
90/10	76	109	127	34	23.8	219	253	48	47.0	23.2
85/15	75	110	129	32	24.2	219	253	49	46.1	21.9
PET/P82										
99/1	77	114	130	30	22.6	221	253	47	43.5	20.9
95/5	74	111	128	31	22.8	219	253	50	44.4	21.6
90/10	74	111	129	36	20.4	219	253	48	40.7	20.3
85/15	74	110	130	36	20.7	219	253	48	40.2	19.5

(b) From Cooling Scans					
Composition	Crystallization				Content of POB (Wt %)
	Onset (°C)	T_c (°C)	ΔT_c (°C)	ΔH_c (J/g)	
PET/P28					
100/0	216	200	37	39.9	0.00
99/1	221	201	37	41.4	0.14
95/5	221	208	33	44.3	0.68
90/10	222	211	30	44.8	1.35
85/15	220	207	30	43.1	2.03
PET/P82					
99/1	220	205	33	43.7	0.71
95/5	221	205	33	43.9	3.56
90/10	218	205	33	41.3	7.12
85/15	217	204	34	38.8	10.68

blending with P28 or P82 at the level of 1–15 wt %. The PET/P28 blend at the 90/10 blending ratio exhibits the most significant acceleration of PET crystallization because of the highest crystallization onset temperature (222°C) and crystallization peak temperature (211°C), the narrowest crystallization width (30°C), as well as the greatest heat of crystallization (44.8 J/g) [Table III(b)]. On the other hand, the PET/P82 blend at the 95/5 blending ratio exhibits the greatest acceleration because of the highest crystallization onset temperature (221°C) and the greatest heat of crystallization (43.9 J/g) [Table III(b)].

Results obtained by Baird et al.⁴ on PET/LCP60 and PET/LCP80 blends indicated that a melt resi-

dence time in the extruder on the order of 4.5–6 min was necessary before any transesterification reaction. In this work, the blending time (8 min) was slightly longer than 4.5–6 min. We believe that some transesterification occurred during the blending process. The relationship between transesterification and PET crystallization will be reported in a later publication.

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

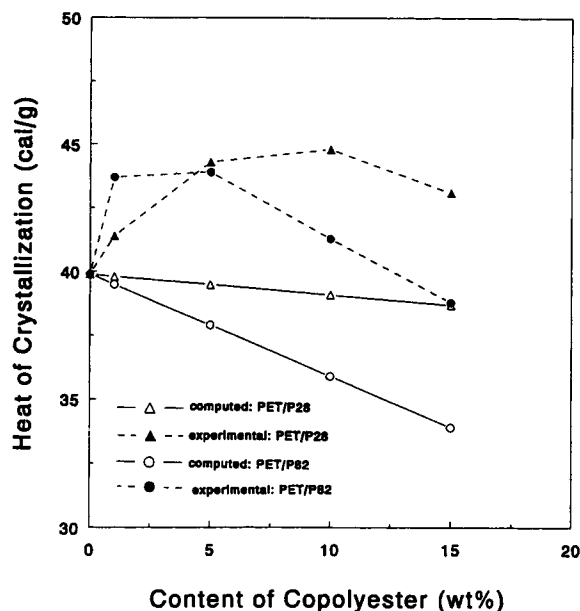


Figure 2 The composition dependence of heat of crystallization PET in the PET/P28 and PET/P82 blends: (—) computed values; (---) experimental values.

present investigation clearly indicate that this modification depends on the physical state (solid or molten), composition, and amount of the second component and on other factors such as chemical interaction between the polymer and the second component. It was found that P28 copolyester accelerates the crystallization rate of PET more significantly than it does the other samples, i.e., P46, P64, and P82, when it is blended into PET at a level of 10 wt %. The PET/P28 blend at a 90/10 blending ratio and the PET/P82 blend at a 95/5 blending

ratio exhibit the fastest crystallization rate over the copolyester content range from 1 to 15 wt %.

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