

The Crystallization Rate of Poly(ethylene terephthalate) Accelerated by Co[poly(butylene terephthalate-*p*-oxybenzoate)] Copolyesters

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ABSTRACT: Poly(ethylene terephthalate) (PET) was blended with three different kinds of co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters, designated B28, B46, and B64, with the level of copolyester 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 samples was then studied via differential scanning calorimetry. The results indicate that these three copolyesters accelerate 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/B28 blends with a maximum level at 10 wt % of B28. The melting temperatures for the blends are comparable with 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 copolyester in the blends. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 587–593, 2000

Key words: crystallization rate; copolyester; blend; liquid crystalline polymer

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

was 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 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 a 85/15 PET/PMMA blend.⁴ 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 an LCP level between 0 and 5 wt %. In the range from 10 to 15 wt %, VLC and KLC

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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, the chemical compatibility, and the degree of dispersion achieved in the mixing process.

In this study, we report the melting and crystallization behavior of a commercial PET resin blended with three types of copoly(butylene terephthalate-*p*-oxybenzoate) copolyesters (PBT-POB). The objective of this investigation was to elucidate the effects of composition and the amount of the copolyester component on the PET crystallization rate.

EXPERIMENTAL

Materials

Three PBT-POB copolyesters, designated B28, B46, and B64, were synthesized according to the procedure reported in our previous study.⁸ These copolyesters contain different POB/PBT molar ratios: 20/80 in B28, 40/60 in B46, and 60/40 in B64. PET was a commercial product from the Far East Textile Co. (Taoyuan, Taiwan), having an intrinsic viscosity of 0.62 (dL/g) measured at 30°C in 60/40 by weight phenol/tetrachloroethane solvent. PET and the copolyesters were dried *in vacuo* at 70°C for 48 h prior to solution blending.

Blending Method

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 in order to remove the phenol/tetrachloroethane solvent completely. The final precipitate was dried completely *in vacuo* at 70°C. Four compositions were prepared with PET/B28 and PET/B64 weight ratios of 99/1, 95/5, 90/10, and 85/15. The PET/B46 were made only at a 90/10 composition. The pure PET was also subjected to identical processing in the phenol/tetra-

chloroethane solvent in order to nullify the effects of thermal history.

DSC Measurement

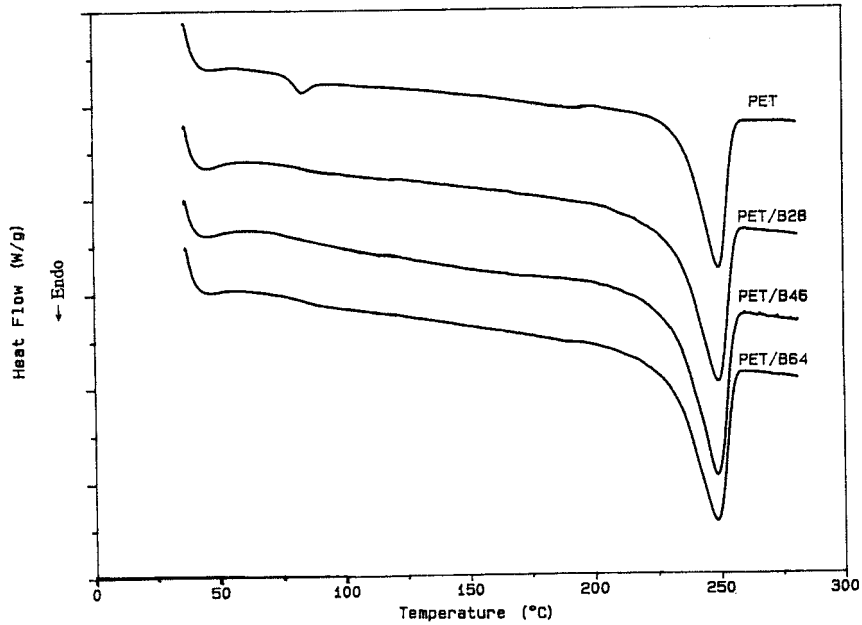
The weight of all samples was kept between 10 and 11 mg for differential scanning calorimetry (DSC) evaluation. DSC measurements were carried out in a DuPont DSC cell equipped with a DuPont 2000 thermal analyst system. Samples were heated to 300°C at a heating rate of 10°C/min under a nitrogen atmosphere, held for 3 min to destroy anisotropy, and then cooled at 10°C/min to 30°C. Both melting and crystallization parameters were obtained from the heating and cooling 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 are referred the whole blends. All results are the average of three samples.

RESULTS AND DISCUSSION

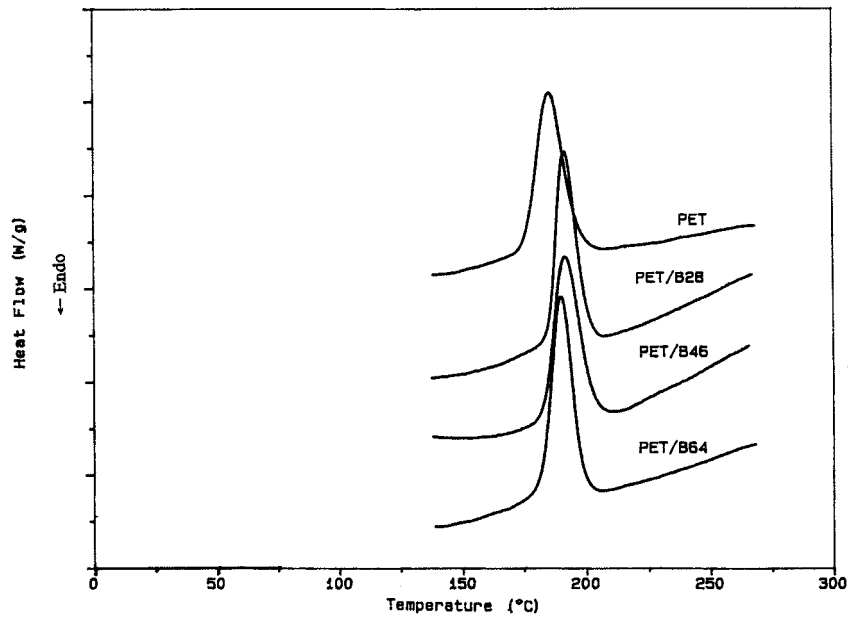
Composition Effect by Blending 10 Wt % Copolyester

The results of DSC heating and cooling scans for PET and PET blends with 10 wt % different copolyesters are shown in Figure 1, (a) and 1(b), respectively. It is evident that there is an endothermic melting peak in all of the heating scan and there is a distinct exothermic crystallization peak in all of the cooling scans. The PET indicates a glass transition at about 75°C in the heating scan. The various melting and crystallization parameters determined from heating and cooling scans for all blends are given in Table I.

The melting temperatures of all blends remain about the same as that of PET (251°C). The onset temperature of melting and melting peak width (ΔT_m) are related to the least stability and distribution of crystallites, respectively. The values of onset temperature of melting and ΔT_m for the PET/B64 blend are found to be comparable with those of pure PET. However, a clear increase of the onset temperature of melting is found in the PET/B28 and PET/B46 blends with respect to that of pure PET. The values of onset temperature of melting for PET/B28 and PET/B46 blends



(a)



(b)

Figure 1 DSC thermograms of PET and PET blends with 10 wt % different copolyesters. (a) Heating scans; (b) cooling scans.

are 8°C higher than that of pure PET (210°C). A clear decrease in ΔT_m is found in the PET/B28 and PET/B46 blends with respect to that of pure PET. The values of ΔT_m for PET/B28 and PET/

B46 blends are 8°C lower than that of pure PET (51°C). These results indicate that the crystallites in the 90/10 PET/B28 and 90/10 PET/B46 blends are more perfect than those found in pure PET.

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

| Composition (90/10) | 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) | $\Delta H_c/\text{Time}$ (J/g s) |
| PET | 210 | 251 | 51 | 32.6 | 205 | 185 | 40 | 27.4 | 0.114 |
| PET/B28 | 218 | 250 | 43 | 34.1 | 208 | 194 | 30 | 28.7 | 0.159 |
| PET/B46 | 218 | 249 | 43 | 28.9 | 208 | 192 | 31 | 24.9 | 0.133 |
| PET/B64 | 211 | 249 | 49 | 32.8 | 205 | 191 | 33 | 26.7 | 0.135 |

But, the lower stability and distribution of PET crystallites in the 90/10 PET/B64 blend are comparable with those found in pure PET.

The crystallization parameters of blends obtained from the cooling scans are given in Table I. A shift in the crystallization onset temperature represents modification of the nucleation process. The crystallization onset temperatures are 3°C higher than that of pure PET (205°C) in the PET/B28 and PET/B46 blends. The crystallization peak temperature (T_c) represents the temperature at the maximum crystallization rate. Also, these temperatures for the blends are higher by 6 to 9°C than that of pure PET (185°C). 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 for the blend are narrower by 7 to 10°C than that of pure PET (40°C). On the other hand, values of ΔH_c for blends are smaller than that of PET (27.4 J/g), except for the PET/B28 blend (28.7 J/g), if the crystallization rate were defined as the heat of crystallization in a unit time ($\Delta H_c/\text{time}$). All the crystallization rates for the blends are greater than that of PET (0.114 J/g s⁻¹). Comparing the values of ΔH_f with those of ΔH_c , the values of ΔH_f are always larger than those of ΔH_c . Because PET crystallizes very slowly from the melts, it will recrystallize in the following heating process.

The crystallization onset temperature and crystallization peak temperature for the 90/10 PET/B28 blend are the highest among all blends. The other hand, 90/10 PET/B28 blend exhibits the narrowest crystallization width (30°C) and the greatest heat of crystallization (28.7 J/g) and crystallization rate (0.159 J/g s) among all blends. These results imply that the crystallization of PET can be accelerated by blending with 10 wt % copolyesters: e.g., B28, B46, and B64. Furthermore, the acceleration of PET crystallization is most pronounced in the 90/10 PET/B28 blend.

Composition Effect by Blending Different Wt % Copolyesters

To confirm the composition dependence of the crystallization of PET in the blends, the PET/B28 and PET/B64 blends were subjected to further studies. Four compositions were prepared in weight ratios of 99/1, 95/5, 90/10, and 85/15. There was a melting endothermic peak in all heating scans, and there was only a distinct crystallization exothermic peak in all the cooling scans, such as Figure 1(a,b). The various melting and crystallization parameters determined from heating and cooling scans are summarized in Table II. It is obvious that onset temperatures of melting, melting temperatures, melting peak widths, and the heat of fusion for the PET/B64 blends are comparable with those of pure PET. This indicates that the lower stability and distribution of PET crystallites does not change by blending with 1, 5, 10, and 15 wt % of B64 copolyester. The other hand, a clear increase (3–8°C) of the onset temperature of melting and a clear decrease (6–8°C) of ΔT_m are found in the PET/B28 blends with respect to those of pure PET. These results indicate that the PET crystallites in the PET/B28 blends with 1–15 wt % of B28 copolyester are more perfect than those found in pure PET.

The composition dependence of the crystallization parameters during cooling for the PET/B28 and PET/B64 blends are given in Table II. The crystallization onset temperatures for PET/B28 and PET/B64 blends are higher than that of pure PET in all four compositions. The values of T_c are shown in Figure 2. The T_c for the PET/B28 and PET/B64 blend systems shows a maximum at ~10 wt % copolyester. The 90/10 PET/B28 blend exhibits the highest T_c among all blends. The ΔH_c is always narrower than that of pure PET (40°C) in all PET/B28 and PET/B64 blends. Some values of ΔH_c for the PET/B28 and PET/B64 blends are

Table II DSC Data of PET Blends with Different Wt % of B28 and B64

| 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) | $\Delta H_c/\text{Time}$ (J/g s) |
| PET/B28 | | | | | | | | | |
| 100/0 | 210 | 251 | 51 | 32.6 | 205 | 185 | 40 | 27.4 | 0.114 |
| 99/1 | 213 | 250 | 43 | 32.1 | 207 | 189 | 34 | 27.8 | 0.133 |
| 95/5 | 217 | 250 | 44 | 33.7 | 208 | 192 | 30 | 28.5 | 0.158 |
| 90/10 | 218 | 250 | 43 | 34.1 | 208 | 194 | 30 | 28.7 | 0.159 |
| 85/15 | 217 | 250 | 45 | 32.3 | 207 | 191 | 31 | 27.2 | 0.146 |
| PET/B64 | | | | | | | | | |
| 99/1 | 210 | 249 | 51 | 31.4 | 205 | 188 | 37 | 27.6 | 0.121 |
| 95/5 | 211 | 250 | 50 | 32.9 | 207 | 190 | 35 | 27.5 | 0.131 |
| 90/10 | 211 | 249 | 49 | 32.8 | 205 | 191 | 33 | 26.7 | 0.135 |
| 85/15 | 210 | 249 | 51 | 31.6 | 206 | 189 | 35 | 26.2 | 0.125 |

smaller than that of pure PET. From the values of ΔH_c for B28 and B64 are 21.5 and 10.7 (J/g),⁹ 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/B28 and PET/B64 blends. These blends exhibit higher experimental ΔH_c than those computed over the entire composition range, indicating that PET is crystallized to a

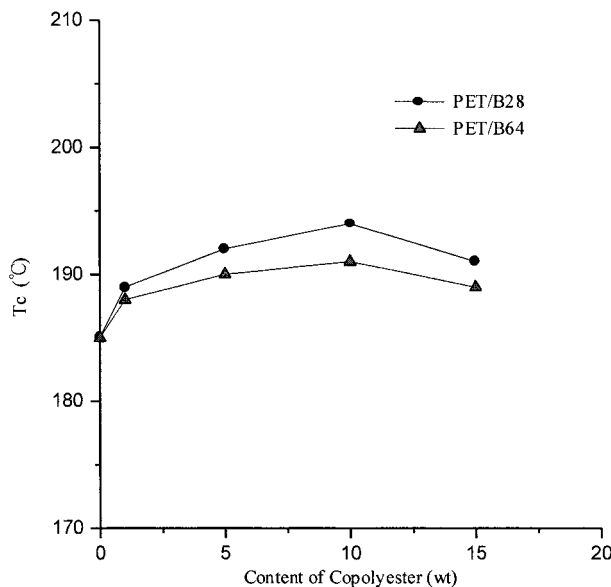


Figure 2 Crystallization temperatures of PET blends with 1–15 wt % of B28 and B64 copolyesters. The point at 0 wt % corresponds to pure PET.

greater extent than expected, by blending with B28 or B64 at the level of 1–15 wt %. The crystallization rates for the PET/B28 and PET/B64 blends are shown in Figure 4. As can be seen in Figure 4, the crystallization rate for the PET/B28 and PET/B64 blends are always greater than that of pure PET. The crystallization rates for the PET/B28 and PET/B64 blends systems shows a maximum at ~10 wt % copolyester. The 90/10 PET/B28 blend exhibits the greatest crystallization rate among all blends. These results reveal that the 90/10 PET/B28 blend exhibits a most significant acceleration of PET crystallization be-

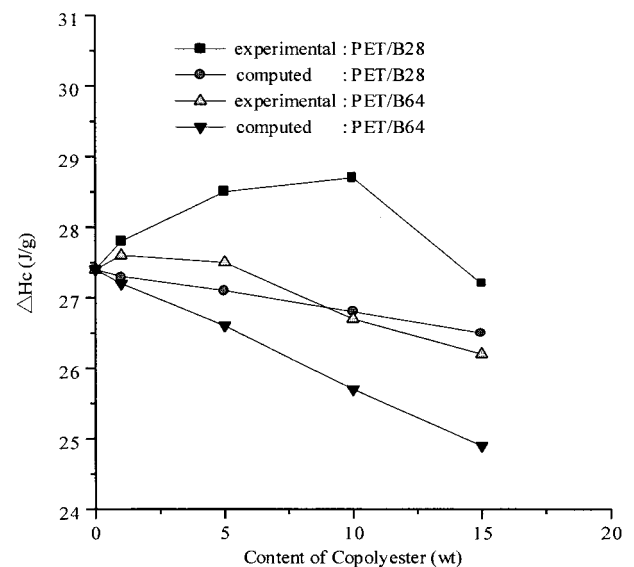


Figure 3 The composition dependence of heat of crystallization PET in the PET/B28 and PET/B64 blends.

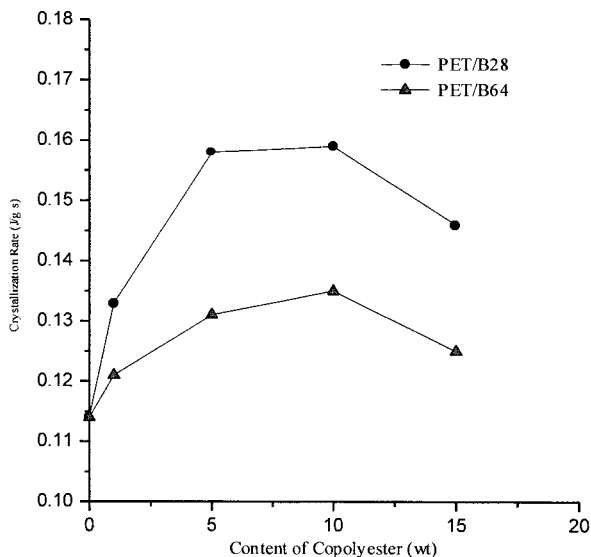


Figure 4 Crystallization rate of PET blends with 1–15 wt % of B28 and B64 copolyesters. The point at 0 wt % corresponds to pure PET.

cause of the highest crystallization onset temperature (208°C) and T_c (194°C), the narrowest ΔH_c (30°C), as well as the greatest ΔH_c (28.7 J/g) and crystallization rate (0.159 J/g s⁻¹) in the PET/B28 and PET/B64 blend systems.

In general, where units of the same chemical structure in two distinct polymer cocrystallize, adjacent and dissimilar units of polymer component in the polyblends can act as impurities and deform the crystal structure.¹⁰ Thus, the 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 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 paper,¹⁶ which investigated the effect of the transesterification 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 do not need to be considered. The crystallization rate of PET was accelerated by blending with the B28, B46, and B64 copolyesters over the content range from 1 to 15%. This may be explained as follows: (1) From the values of crystallization temperatures of B28, B46, and B64, which are 185, 164, and 154°C,⁹ respectively, PET crystallizes in the presence of the melts of this second component. The melts of these copolyesters, which exhibit a high degree of molecular order of the anisotropic phase, even the liquid crystalline B46 and B64, accelerate the nucleation and growth process in a manner similar to that of a nucleating agent. (2) From the results of our previous paper,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. The blend with 1–2 wt % exhibits the narrowest crystallization width and the greatest heat of crystallization in the PET/P28, PET/P46, and PET/P82 blends at 90/10 composition. In this research, the 90/10 PET/B64 blend exhibits perhaps a greater extent of transesterification during the heating scan, owing to the POB content that is larger than those of 90/10 PET/B28 and 90/10 PET/B46 blends. Thus, the acceleration of PET crystallization was not as significant as it was in the 90/10 PET/B28 and 90/10 PET/B46 blends.

In our previous research,¹⁸ the compatibility and interfacial adhesion between PET and PET-POB copolyesters are dependent on the composition of the copolyesters. Two-phase morphology was observed by scanning electron microscopy (SEM). It was observed that the greater the similarity between copolyester and PET in blends, the better miscibility or interfacial adhesion between the two phases. The PET/P28 blend indicates the best interfacial adhesion and miscibility, owing to the best similar composition between PET and P28. In this research, the composition and structure of PBT-POB copolyester are similar to that of PET-POB copolyester. We believe that the morphology of blend and the miscibility between PET and PBT-POB copolyester would be similar to PET/PET-POB blend. The PET/B28 blend exhibits the best interfacial adhesion and miscibility among all the PET/PBT-POB blends. One of the reasons that 90/10 PET/B28 blend exhibits the most significant acceleration of PET

crystallization is because it has the best miscibility among all blends.

CONCLUSION

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 B28 copolyester accelerates the crystallization rate of PET more significantly than the other samples, i.e., B46 and B64, when it is blended into PET at a level of 10 wt %. The 90/10 PET/B28 blend exhibits the fastest crystallization rate over the copolyester content range from 1 to 15 wt % among all PET/B28 and PET/B64 blends.

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