

The crystallization behaviors of poly(butylene terephthalate) blended with co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters

Cheng-Fang Ou^{*}, Min-Shiun Chao, Shih-Liang Huang

Department of Chemical Engineering, National Chin-Yi Institute of Technology, Taichung, Taiwan, ROC

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Abstract

Poly(butylene terephthalate) (PBT) was blended with three different kinds of co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters, designated B28, B46, and B64, with the copolyester level varying from 2 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 by DSC. The results indicate that these three copolyesters accelerate the crystallization rate of PBT in a manner similar to that of a nucleating agent. The acceleration of PBT crystallization rate was most pronounced in the PBT/B28 blends with a maximum level at 10 wt.% of B28. The melting endotherm onset temperatures and the melting peak widths for the blends are comparable with those of pure PBT. These results imply that the stability of PBT crystallites in the blends is not significantly influenced by blending. The observed changes in crystallization behavior are explained by the effect of the composition and the amount of copolyester in the blends. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Crystallization rate; Copolyester; Blend; Liquid crystalline polymer

1. Introduction

Polybutylene terephthalate (PBT), a high-performance, semicrystalline resin, is one of the toughest and the most versatile of all engineering thermoplastics. Continued technological developments in alloying have extended the capabilities of the basic PBT resins and have led to an expanded acceptance in materials consuming industries [1]. In order to enhance the ease of processing and crystallization rate, the crystallization behavior of this resin must be more intensively investigated.

On the other hand, polymer blends have recently become attractive both for industrial application and

academic interest. They are more convenient for developing new polymers than starting from monomer synthesis and polymerization. Moreover, blending can improve properties and processibility of existing polymers and reduce the cost to achieve performance/price balance. The inherent properties of the individual polymer components, the mode of dispersion, the shape, size, and orientation of phases, their interaction, and volume fractions are all important factors of the blend's behavior. Most of the researches on the PBT blends were concerned with the compatibility [2–8]. The phase behavior of co[poly(ethylene terephthalate-*p*-oxybenzoate)] (POB–PET)/PBT blend as revealed by differential scanning calorimetry (DSC) and dynamic mechanical measurement is reported by Kimura and Porter [9] and Zadula and coworkers [10], respectively. However, in view of the crystallization in our previous study [11], we have found that an addition of the POB–PET copolyesters can accelerate the crystallization rate of PBT in a

^{*} Corresponding author. Tel.: +886-4-393-9018; Fax: +886-4-392-7861.

E-mail address: oucf@chinyi.ncit.edu.tw (C.-F. Ou).

manner similar to a nucleating agent. As a result, the crystallization behavior of PBT in the blends might be influenced by the composition and amount of the copolyester blended.

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

2. Experimental

2.1. Materials

Three POB–PBT copolyesters, designated B28, B46, and B64, were synthesized according to the procedure reported in our previous study [12]. These copolyesters contain different POB/PBT molar ratios: 20/80 in B28, 40/60 in B46, and 60/40 in B64. PBT was a commercial product from the Far East Textile Co. (Taoyuan, Taiwan) having an intrinsic viscosity of 1.0 (dl/g) measured at 30°C in 60/40 by weight phenol/tetrachloroethane solvent. PBT and the copolyesters were dried in vacuo at 70°C for 48 h prior to solution blending.

2.2. Blending method

The solution blends of different compositions employed were prepared by dissolving an amount of PBT/copolyester in the desired weight ratio in 60/40 by weight phenol/tetrachloroethane solvent at 50°C. These solutions were stirred for 3 h and then added dropwise to an 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 PBT/B28 and PBT/B64 weight ratios of 98/2, 95/5, 90/10, and 85/15. The PBT/B46 were made only at a 90/10 composition. The pure PBT was also subjected to identical processing in the phenol/tetrachloroethane solvent in order to nullify the effects of thermal history.

2.3. Differential scanning calorimetry

The weight of all samples was kept between 10 and 11 mg for 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 thermal 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. The heat of fusion (ΔH_f) and crystallization heats (ΔH_c) were determined from the areas of melting peaks and crystallization peaks.

3. Results and discussion

3.1. Composition effect by blending 10 wt.% copolyester

The results of DSC heating and cooling scans for PBT and PBT blends with 10 wt.% different copolyesters are shown in Fig. 1(a) and (b), respectively. It is evident that there is an endothermic melting peak in all the

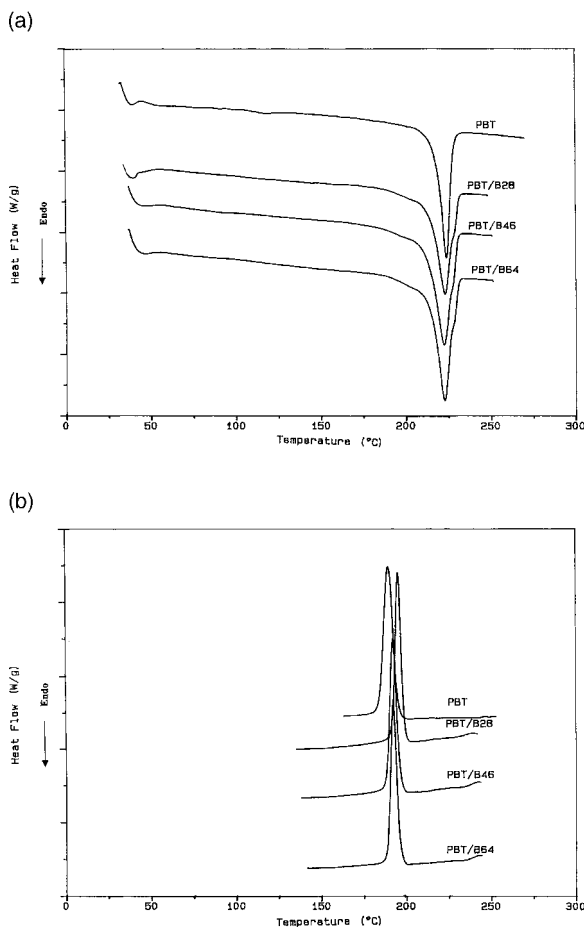


Fig. 1. DSC thermograms of the PBT and PBT blends with 10 wt.% of different copolyesters: (a) heating scans and (b) cooling scans.

Table 1
DSC data of PBT and PBT blends with 10 wt.% of 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)	ΔT^a (°C)
PBT	203	223	33	36.9	203	189	22	37.2	0.282	34
PBT/B28	203	222	32	35.3	203	196	19	36.2	0.318	26
PBT/B46	203	222	32	37.3	202	193	20	37.1	0.309	29
PBT/B64	203	223	32	36.5	202	193	20	35.9	0.299	30

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

heating scans, and there is a distinct exothermic crystallization peak in all the cooling scans. The various thermal and crystallization parameters determined from heating and cooling scans for all blends are given in Table 1.

The melting temperatures of all blends were kept about the same as that of PBT (223°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 all blends are found to be comparable with those of pure PBT. These results indicate that the least stability and distribution of PBT crystallites in the blends are comparable with those found in pure PBT.

The parameters characterizing the nonisothermal crystallization behavior of blends obtained from the cooling scans are summarized in Table 1. A shift in the crystallization onset temperature represents modification of the nucleation process. It is clear that the nonisothermal crystallization behavior of PBT is not altered significantly by blending with 10 wt.% copolyesters, in terms of the onset temperature of crystallization. The crystallization peak temperature (T_c) represents the temperature at maximum crystallization rate. Also, these temperatures for the blends are higher by 4°C to 7°C than that of pure PBT (189°C). However, the crystallization peak width (ΔT_c), which is the range over which the blend crystallizes. 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 ΔT_c for the blend is narrower by 2°C to 3°C than that of pure PBT (22°C). The heat of crystallization (ΔH_c) for blends is lower than that of PBT (37.2 J/g). If the crystallization rate were defined as the heat of crystallization divided by time, which is from the onset to the completion of crystallization ($\Delta H_c/\text{time}$). The crystallization rate for the blends is greater than that of PBT (0.282 J/g s) as seen in Table 1. In programmed cooling, the crystallization temperature reflects the overall crystallization rate due 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, i.e., the smaller the ΔT , the higher the overall crystallization rate. The ΔT for the blends are smaller by 4–8°C than that of the pure PBT (34°C). The result again reveals that the overall crystallization rate for the blends is greater than that of PBT.

The crystallization peak temperature for the 90/10 PBT/B28 blend (196°C) is the highest among all blends. On the other hand, the 90/10 PBT/B28 blend exhibits the narrowest crystallization width (19°C), the greatest $\Delta H_c/\text{time}$ (0.318 J/g s) and the smallest degree of supercooling (26°C) among all blends. These results imply that the crystallization of PBT may be accelerated by blending with 10 wt.% copolyesters: e.g., B28, B46, and B64. Furthermore, the acceleration of PBT crystallization is the most pronounced in the 90/10 PBT/B28 blend.

3.2. Composition effect by blending different wt.% copolyester

To confirm the composition dependence of the crystallization of PBT in the blends, the PBT/B28 and PBT/B64 blends were subjected to further studies. Four compositions were prepared in weight ratios of 98/2, 95/5, 90/10, and 85/15. There was a melting endothermic peak in all the heating scans, and there was only a distinct crystallization exothermic peak in all the cooling scans as shown in Fig. 1(a) and (b). The various thermal and crystallization parameters determined from heating and cooling scans are summarized in Table 2. It is obvious that onset temperatures of the melting, melting temperatures, melting peak widths, and the heat of fusion for the PBT/B28 and PBT/B64 blends are comparable with those of pure PBT. This indicates that the least stability and distribution of PBT crystallites does not change by blending with 2, 5, 10, and 15 wt.% of B28 and B64 copolyester.

The composition dependence of the crystallization parameters during cooling for the PBT/B28 and PBT/B64 blends are given in Table 2. The crystallization onset temperatures for the PBT/B28 and PBT/B64 blends are comparable with that of pure PBT in all four compositions. The values of T_c are shown in Fig. 2. The T_c for the PBT/B28 and PBT/B64 blends systems show a

Table 2
DSC data of PBT 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)	ΔT^a (°C)
<i>PBT/B28</i>										
100/0	203	223	33	36.9	203	189	22	37.2	0.282	34
98/2	203	223	33	37.3	204	194	22	37.8	0.286	29
95/5	201	223	34	38.9	203	195	21	37.4	0.297	28
90/10	203	222	32	35.3	203	196	19	36.2	0.318	26
85/15	202	223	32	35.4	203	195	21	34.5	0.274	28
<i>PBT/B64</i>										
98/2	203	223	32	36.8	203	193	21	36.9	0.293	30
95/5	202	223	32	36.3	203	193	21	36.4	0.289	30
90/10	203	223	32	36.5	202	194	20	35.9	0.299	29
85/15	202	222	33	35.1	202	192	21	33.0	0.262	30

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

maximum at ~10 wt.% copolyester. The 90/10 PBT/B28 blend exhibits the highest T_c among all blends. The ΔT_c are always narrower by 1°C to 3°C than that of pure PBT (22°C) in all the PBT/B28 and PBT/B64 blends. Some values of ΔH_c for the PBT/B28 and PBT/B64 blends are smaller than that of pure PBT. From the values of ΔH_c for B28 and B64 are 21.5 and 10.7 J/g [13], 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 Fig. 3, where computed and experimental results are compared for the PBT/B28 and PBT/B64 blends. These blends exhibit a higher experimental ΔH_c than those computed over the level of 1–10

wt.% of copolyesters, indicating that the PBT is crystallized to a greater extent than expected, by blending with B28 or B64 at the level of 1–10 wt.%. But the values of experimental ΔH_c are smaller than those of computed ΔH_c for the blends with 15 wt.% B28 or B46. As can be seen in Fig. 4, the $\Delta H_c/\text{time}$ for the PBT/B28 and PBT/B64 blends is always greater than that of pure PBT. The $\Delta H_c/\text{time}$ for the PBT/B28 and PBT/B64 blends systems shows a maximum at ~10 wt.% copolyester. The ΔT given in Table 2 for the PBT/B28 and PBT/B64 blends systems are smaller by 4–8°C than that of pure PBT (34°C). The 90/10 PBT/P28 blend exhibits the smallest ΔT (26°C). These results reveal that the overall crystallization rate for the blends are greater than that of

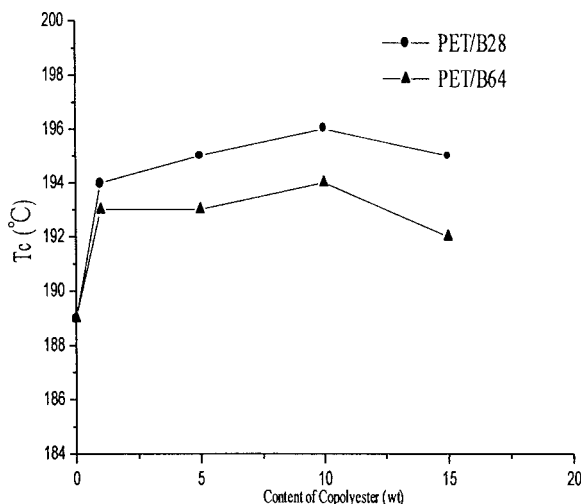


Fig. 2. Crystallization temperatures of PBT blends with 1–15 wt.% of B28 and B64 copolyesters. The point at 0 wt.% corresponds to pure PBT.

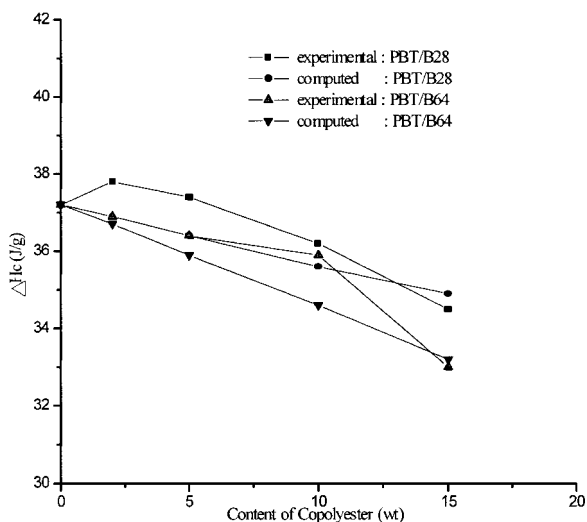


Fig. 3. The composition dependence of heat of crystallization PBT on the PBT/B28 and PBT/B64 blends.

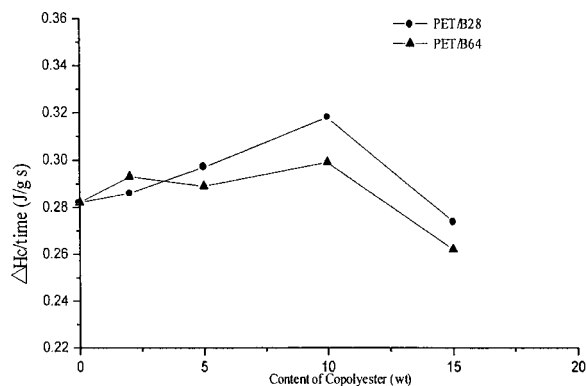


Fig. 4. The $\Delta H_c/\text{time}$ of PBT blends with 1–15 wt.% of B28 and B64 copolyesters. The point at 0 wt.% corresponds to pure PBT.

PBT. From the results of ΔH_c and crystallization rate, it seems that small quantities (less than 10 wt.%) of B28 and B64 copolyesters could act as nucleating agents for PBT resin, but large quantities (greater than 15 wt.%) of B28 and B64 will destroy the symmetry of PBT, and result in decreases of the ΔH_c and crystallization rate.

The 90/10 PBT/B28 blend consisting of 1.2 wt.% oxybenzoate exhibits the most significant acceleration of PBT crystallization because of the highest crystallization temperature (196°C), the narrowest ΔT_c (19°C), the greatest $\Delta H_c/\text{time}$ (0.318 J/g s) as well as the smallest ΔT in the PBT/B28 and PBT/B64 blends 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 [14]. Thus, the depression of values of T_m and ΔH_f with blend composition is often observed. The retardation of the PET crystallization and lowering of its degree of crystallinity and crystallization rate in miscible blends of PET/PAr have been reported [15–19]. The decrease in the crystallinity of these blends was attributed to the inclusion of the rigid PAr unit in PET chains, which cause a decrease in their crystallizable segment length. In our previous paper [20], which investigate the effect of the transesterification in the 50/50 PET/P46 blend after different times reveals that the crystallization rate decrease 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 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, since the absence of transesterification was confirmed by NMR measurement on the blend made before and after solution blending, the effect of transesterification on the crystallization rate

of PBT blends does not need to be considered. The PBT exhibits a rapid crystallization rate. A high injection molding speed is generally recommended. The crystallization rate of PBT was accelerated by blending with the B28, B46 and B64 copolyesters over the content range from 1% to 10%. This may be explained as follows: from the T_c of PBT and copolyesters, PBT crystallizes in the presence of the melts of these second component. It seems that the copolyester content less than 10 wt.% may not destroy the symmetry of PBT that result in the decrease of crystallization. But the dispersed droplet melts of these copolyester, which exhibit high degree of molecular order of anisotropic phase even liquid crystalline (B46 and B64) increases the nucleating spot and accelerates the nucleation and growth process in a manner similar to that of a nucleating agent.

4. 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 amount of the second component. It was found that B28 copolyester accelerates the crystallization rate of PBT more significantly than the other samples, i.e. B46, and B64, when it is blending into PBT at a level of 10 wt.%. The 90/10 PBT/B28 blend exhibits a most significant acceleration of PBT crystallization over the copolyester content range from 1 to 15 wt.% among all the PBT/B28 and PBT/B64 blends.

References

- [1] Margolis JM, editor. Engineering thermoplastic: properties and applications. New York: Marcel Dekker, 1985 [Chapter 2].
- [2] Devaux J, Goddard P, Mercier JP. *J Polym Sci Polym Phys Ed* 1982;20:1901.
- [3] Wahrmund DC, Paul DR, Barlow JW. *J Appl Polym Sci* 1978;22:2155.
- [4] Velden Gvd, Smitsmans KG, Veermans A. *Polym Commun* 1987;28:169.
- [5] Hobbs SY, Groshans VL, Dekkers ME, Shultz AR. *Polym Bull* 1987;17:335.
- [6] Birley AW, Chen XY. *Br Polym J* 1984;16:77.
- [7] Kimura M, Porter RS. *J Polym Sci Polym Phys Ed* 1983;21:367.
- [8] Robeson LM, Furtek AB. *J Appl Polym Sci* 1979;23:645.
- [9] Kimura M, Porter RS. *J Polym Sci Polym Phys Ed* 1984;22:1697.
- [10] Zadula A, Munoz E, Pena JJ, Santamaria A. *Polymer* 1991;32:682.
- [11] Song WJ, Ou CF, Lin CC. *J Appl Polym Sci* 1996;60:1505.

- [12] Ou CF. *J Appl Polym Sci*, in press.
- [13] Ou CF. *J Appl Polym Sci*, in press.
- [14] Lenz RW, Jin JI, Feichtinger KA. *Polymer* 1983;24:327.
- [15] Kimura M, Salee G, Porter RS. *J Appl Polym Sci* 1984;29:1629.
- [16] Eguiazabal JI, Calahorra ME, Cortazar MM, Iruin JJ. *J Polym Engng Sci* 1984;24:608.
- [17] Eguiazabal JI, Ucar G, Cortazar M, Iruin JJ. *Polymer* 1986;27:2013.
- [18] Eguiazabal JI, Cortazar M, Iruin JJ. *J Appl Polym Sci* 1991;42:489.
- [19] Martinez JM, Nazabal J, Eguiazabal JI. *J Appl Polym Sci* 1994;51:223.
- [20] Ou CF, Lin CC. *J Appl Polym Sci* 1996;61:1455.