Crystallization Behavior of PBT/ABS Polymer Blends

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ABSTRACT: Poly(butylene terephthalate) (PBT) crystallization behavior is modified by blending it with acrylonitrile-butadiene-styrene copolymers (ABS). The effects of ABS on melting and crystallization of PBT/ABS blends have been examined. Most ABS copolymers of different rubber content and styrene/acrylonitrile ratios studied showed little effect on the melting behavior of PBT crystalline phase. However, ABS copolymer with high acrylonitrile content had a significant effect on the crystallization behavior of the PBT/ABS blends. The nucleation rate of the PBT crystalline phase decreased due to the presence of the high acrylonitrile content ABS, whereas the spherulitic growth rate increased significantly. These phenomena are attributed to changes in nucleation and growth mechanisms of PBT crystalline phase promoted by ABS. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 423–430, 1999

Key words: crystallization; polymer blends; poly(butylene terephthalate); acrylonitrile-butadiene-styrene copolymers

INTRODUCTION

Poly(butylene terephthalate) (PBT) is an important engineering thermoplastic that requires the addition of impact modifiers to enhance its performance under impact resistance tests, mainly for notched test specimens. Different types of polymers have been blended with PBT to improve its toughness.^{1–3} PBT, a semicrystalline polymer, shows a high rate of crystallization, which improves its performance in the manufacturing of injection-molded articles.⁴ It has been shown that blends of PBT with other polymers may induce drastic changes in the crystallization behavior of PBT.⁵⁻¹¹ Addition of copolyester based on bisphenol-A to PBT induces a depression in the melting temperature and a decrease in the degree of crystallinity of PBT. Furthermore, spherulites of PBT in the blends were found to be coarser than those in PBT homopolymer.⁶ Phenoxi reduces the PBT

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crystallization rate. However, surprisingly, it induces a higher degree of crystallinity in PBT.⁷ Bisphenol-A polycarbonate (PC) does not affect the degree of crystallinity of PBT, despite generating a partially miscible blend with a slightly lower melting temperature for PBT.^{8,9} Polyacrylate modifies the kinetics of crystallization of PBT, leading to preferential crystallographic directions of crystal growth.^{10,11}

Impact modifiers do not seem to induce significant changes in PBT crystallization behavior. The addition of methacrylate-butadiene-styrene copolymer (MBS), a core-shell impact modifier, does not significantly change the melting and the crystallization behavior of PBT in the blends.¹² Unfortunately, there is little information in the literature about the effect of impact modifiers on the melting and crystallization behavior of PBT. Functionalized ethylene-propylene rubbers (EPR) do not change the melting temperature of PBT; however, they do reduce the degree of crystallinity of PBT in the blends.¹³

Acrylonitrile-butadiene-styrene (ABS) has been used as an impact modifier for poly(vinyl chloride)

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Materials	Chemical composition			Molecular weight		
	Acrylonitrile (% w/w)	Butadiene (% w/w)	Styrene (% w/w)	$\overline{\frac{M_n}{(\text{g mol})}}$	$\overline{M_w} \\ (\text{g mol})$	$\overline{M_w}/\overline{M_n}$
ABS-1	22	25	53			
ABS-2	23	19	58			
ABS-3	33	14	48			
PBT				20.800	99.300	4.8

Table I Characteristics of the Materials Used in this Study

(PVC), PC, and polyamides.^{2,3,14} Despite the fact that ABS has been used as a toughening agent for PBT for some time,¹⁵ a more scientific approach to the development of PBT/ABS blends has been developed only recently.^{16,17} Thus, very little information on the effect of ABS on the crystallization behavior of PBT can be found in the literature.

In this article, blends of PBT and ABS copolymers of different chemical compositions were studied. The crystallization and melting behavior of PBT in the blends were explored; the results contribute to the understanding of this important phenomena in the PBT material resulting from the addition of an impact modifier such as ABS.

EXPERIMENTAL

Table I displays the properties of the PBT and ABS materials used in this study. The PBT, designated as Valox 315, was supplied by GE Plastics South America (Campinas, Brazil). The ABS resins, designated ABS-810, ABS-830, and ABS-840, were supplied by Nitriflex S.A. (São Paulo, Brazil). The Valox 315 and the ABS resins were designated as PBT, ABS-1, ABS-2, and ABS-3 (see Table I). Table II presents information on the phase composition of the ABS copolymers.

Table II Phase Composition of the ABS

	ABS phase contents (% w/w)			
Phase	ABS-1	ABS-2	ABS-3	
Rubbery phase	29	21	21	
SAN matrix	67	72	73	
Styrene/acrylonitrile				
ratio	72/28	75/25	71/29	
Grafted SAN				
in the SAN phase	67	8	72	

The PBT/ABS blends were prepared in a corotating twin-screw extruder (Werner-Pfleiderer Model ZSK-30) at 230°C and 270 rpm. All materials were dried for a minimum of 4 h at 80°C in a circulating air oven before the melt processing. Samples for the dynamic mechanical thermal analysis (DMTA) and the scanning electron microscopy analysis (SEM) were prepared by injection molding process at 230°C, with a mold temperature of 70°C. Samples for the calorimetric analysis, optical microscopy tests, and X-ray diffraction tests were taken from the melt-extruded pelletized material ground into fine particles. For the optical microscopy observations, thin films were prepared by hot pressing the fine powder between glass slides at 245°C, under conditions of constant load (1.5 kg) and time (30 sec)for all of the samples, after which the films obtained were allowed to cool slowly on the bench. By using this procedure, no significant variation in thickness was observed—a maximum of 12% variation for the films with an average thickness of 30 μ m. The heat treatment on these samples was performed in the hot stage, where they were heated to 260°C and kept at this temperature for 2 min, quenched to 215°C and kept at this temperature for 2 min, and finally quenched to room temperature. The state of miscibility of the PBT/ABS blends was studied with a DMTA from Polymer Laboratories at 3°C/min and a frequency of 1 Hz. The phase morphologies of the blends were characterized by SEM using a Cambridge Stereoscan S4-10. Specimens were obtained by cryofracturing impact test bars and etching the fractured surface with a $10M \operatorname{Cr}_3O_4$ solution at 40°C for 5 min to remove the ABS phase.

The melting and crystallization behavior of the blends were studied by calorimetry using a TA Instruments DSC 2910, heating and cooling rates of 10 and 20°C/min, respectively. The spherulitic morphology of the blend was observed using a polarized Carl Zeiss transmission optical microscope (Model Jenaval) and a hot stage from Lin-

Composition PBT/ABS	T_m	ΔH_f	T_{c}	ΔH_c
(% by weight)	(°C)	(J/g)	(°Č)	(J/g)
PBT				
100	224	46	185	49
PBT/ABS-1				
90/10	224	44	182	49
75/25	225	46	181	47
50/50	224	44	177	46
PBT/ABS-2				
90/10	224	45	183	49
75/25	223	45	180	45
50/50	224	46	178	46
PBT/ABS-3				
90/10	225	45	182	45
75/25	225	44	183	44
50/50	224	46	178	42

Table IIIMelting and CrystallizationParameters for PBT/ABS Blends,Measured by DSC

 T_m = Melting temperature of the PBT crystalline phase; T_c = Crystallization temperature of the PBT; ΔH_f = Heat of fusion of the PBT crystalline phase; ΔH_c = Heat of crystallization of the PBT crystalline phase.

kan Scientific Instruments (Model THM 600). Wide-angle X-ray diffraction (WAXD) was used to characterize the crystalline structure of the blends. A X-ray diffractometer from Carl Zeiss/ Jena (Model HZ64), with a cobalt source (K $\alpha \lambda$ = 1.79 Å), was used to obtain the diffractograms.

RESULTS AND DISCUSSION

Table III gives melting and crystallization characteristics of PBT/ABS blends. Both the melting temperature (T_m) and heat of fusion (ΔH_f) of PBT were not significantly affected by the presence of ABS. Melting point depression was not observed; therefore, PBT and ABS do not show strong evidence of miscibility in the melt state, as predicted by T_m depression miscibility criterion.¹⁹ On the other hand, some evidence of miscibility was found from the properties of the amorphous phase of PBT and the styrene-acrylonitrile (SAN)-rich phase of ABS in the solid state, as observed from the data in Table IV. Different effects were observed from adding ABS to PBT, according to the characteristics of the ABS. The data from Table IV show that ABS-3 alters the $T_{\rm g}$ of PBT at all PBT/ABS blend compositions, although the T_g of ABS-3 was not changed by the presence of PBT. The T_{σ} of each component in the blends PBT/ ABS-1 and PBT/ABS-2 was changed by the presence of the other. Figure 1 shows a multiphase morphology for the PBT/ABS-3 blends. The blends with 10 and 25% by weight of ABS-3 show a well-defined rubbery-phase disperse in the matrix. The rubbery phases of the ABS were extracted by etching and are observed as holes in the micrographs. PBT/ABS blends with equal amounts by weight (50/50) showed an aspect of co-continuous phases.

The crystallization temperature, T_c , of the PBT crystalline phase is depressed by the presence of ABS in the blends (see Table III). Each type of ABS reduces the crystallization temperature of the PBT phase compared to that of neat PBT. The heat of crystallization (ΔH_c) of PBT was markedly affected by the presence of ABS-3 compared to the other ABS grades (see Table III). The decrease in ΔH_c is evidence of suppression of the PBT crystallization. The effect of ABS-3 on the isothermal crystallization of PBT/ABS blends

Table IV Glass Transition Temperatures of PBT/ABS Blends, Measured by DMTA

Composition PBT/ABS (% by weight)	ABS-1		ABS-2		ABS-3	
	T_{g} PBT (°C)	T_{g} ABS (°C)	$T_{g} \ \mathrm{PBT} \ (^{\circ}\mathrm{C})$	T_{g} ABS (°C)	T_g PBT (°C)	T_g ABS (°C)
100/0	60		60		60	
90/10	61	109	61	107	64	119
75/25	62	109	62	108	63	118
50/50	60	110	63	107	64	118
0/100		113		110		119

 T_g ABS = glass transition temperature of the SAN-rich phase of ABS.



Figure 1 SEM micrographs for PBT/ABS blends: (a) 10% w/w ABS-3; (b) 25% w/w/ABS-3; (c) 50% w/w

ABS-3.

can be visualized from the spherulitic morphology observed by polarized light optical microscopy, as shown in Figure 2. All of the samples were prepared by hot pressing the polymer in powder form between glass slides at 250°C. Each slide was heated in the hot stage to 260°C for 2 min. After the previous thermal history was removed, the samples were cooled to 215°C and held at this temperature for another 2 min to allow isothermal crystallization. As a final step, the samples were quenched at approximately 100°C/min.

Considering that all of the samples were allowed to crystallize for an identical period (i.e., 2 min), it can be concluded that the nucleation rate of the spherulites in the blends was lower than in the neat PBT, whereas the spherulite growth rate was higher in the blend. The number of spherulites is smaller, and they grow to a larger size. A large number of very small spherulites could be observed in the background of the spherulitic morphology for the blends [Fig. 2(b-d)]. Those spherulites were nucleated and grown during the quenching step just after isothermal crystallization. They are not considered in this discussion. A previous study²⁰ showed that for isotactic polypropylene (i-PP) a decrease in nucleation rate occurs due to the addition of atactic polypropylene (a-PP). The presence of a-PP reduces the heterogeneous nucleation rate of i-PP, thereby suppressing the number of nuclei. This analogy could not be applied to the PBT/ABS behavior, because i-PP/a-PP is a miscible blend in the melt whereas PBT/ABS is not, as previously discussed. In fact, PBT/ABS blends were found to be immiscible, with enough interfacial area to induce heterogeneous nucleation.

The nucleation rate of a semicrystalline polymer depends partly on the melt viscosity at the crystallization temperature and mainly on the energy barrier to form stable nuclei for further crystal growth.²² The presence of a second immiscible phase in a polymer blend can reduce the energy barrier due to the positive contribution of the interfacial energy that facilitates nuclei formation. The ABS promotes a well-defined interfacial region in the blend, as observed in Figure 1. On the other hand, ABS has a higher melt viscosity than PBT, which increases the melt viscosity of the blend.¹⁷ An increase in viscosity reduces the probability to form nuclei due to the loss of molecular mobility. Therefore, the presence of ABS may increase or decrease nuclei formation rate depending on which effect is more effective on the overall nucleation rate. According to these considerations, it is reasonable to assume that the effect of melt viscosity overcomes the interfacial energy due to the presence of ABS in the polymer blend.



(a)

(b)



Figure 2 Spherulitic morphology for PBT/ABS blends under crystallization: (a) PBT; (b) 10% w/w ABS-3; (c) 25% w/w ABS-3; (d) 50% w/w ABS-3.

The spherulites in the blend were larger than those in the neat PBT, under the same crystallization conditions (Fig. 2). Therefore, it can be concluded that the spherulite growth rate is higher in the blend than in PBT. This behavior is unexpected. Several blends have been studied with respect to spherulite growing rate^{20,22-25}; however, no observation of higher growth rate for the blends than for the neat crystalline component has been made. In fact, almost all of the blends studied have a lower rate than the pure crystallizable component. The lower spherulite growth rate for those blends is attributed to diffusion mechanisms that delay the growth process. As mentioned earlier, addition of ABS to PBT increases the melt viscosity of the polymer blend. Higher viscosity at the crystallization temperature leads to lower diffusion coefficient for the crystallizing molecules, which decreases the crystal growth rate. Therefore, the overall spherulite growth of PBT in the PBT/ABS blend should occur at a lower rate.¹⁰ On the other hand, the addition of ABS affects the crystalline microstructure of PBT in the blends. Figure 3 shows X-ray diffractograms forPBT and its blends. The intensity of the diffraction peaks decreases as ABS is added to the blends. Peaks at approximately 20 and 27° show unique behavior. The intensity of the peak at 27° is lower than the intensity at 20° for the blends, but it is higher for the neat PBT. It has been shown^{26,27} that these two peaks represent diffractions of the (010) and (100) crystal planes, respectively, for PBT. Crystals of PBT show distinct faceting, with the faces being bounded by (010), (100), and (110) planes.²⁸ The long edges of the lamellae are parallel to (010)



(a)



(b)



(c)

Figure 3 X-ray diffractions of PBT/ABS blends: (a) PBT; (b) 25% w/w ABS-3; (c) 50% w/w ABS-3.

planes and to the [210]* reciprocal lattice direction. Usually, PBT spherulites are built up by radial growth of lamellar crystals. The preferential direction for the lamellar growth coincides with the radial spherulite direction; that is [210]. This type of spherulite is known as normal. There is another preferential reciprocal lattice direction for PBT crystal growth: [111]*. The spherulites grown in this direction are referred to as abnormal. The main difference in morphology of these spherulites is related to the position of the Maltese cross with respect to the polarizer and analyser. In normal spherulites the arms of the Maltese cross extinction pattern are coincident with the polarizer and analyzer directions. On the other hand, abnormal spherulites show the extinction arms at 45° with respect to the polarizer and analyzer directions. PBT spherulites also show another important characteristic: the birefringence can be negative or positive when a compensator is used to observe spherulites between polarizer and analyzer.²⁹ Positive spherulites are observed when the polymer chains are parallel to the spherulite radius, whereas negative spherulites are observed when the polymer chains are perpendicular to the spherulite radius. The compensator shows positive spherulites with a darker color in the first and third quadrants with respect to the Maltese cross and negative spherulites with a darker color in the second and fourth quadrants.

Most of the spherulites observed in the neat PBT [Fig. 3(a)] were considered normal, because the arms of the Maltese cross coincide with the polarizer and analyzer positions. In addition, a mixture of positive and negative spherulites was observed by checking the darker color in the Maltese cross quadrants. As ABS was added to PBT, a significant change in the spherulite morphologies was noticed [Fig. 3(b-d)]. Besides enlargement of the spherulites, the well-defined mixture of positive and negative spherulites changed to an intermediate spherulitic morphology. The birefringence of each spherulite became a mixture of positive and negative characteristics [Fig. 3(b)]. In addition, some of the spherulites showed a rotation in the extinction arms of the Maltese cross with respect to the polarizer and analyzer directions. This was evidence of the abnormal spherulites. Thus, the presence of ABS in the crystallization of PBT/ABS blends induced a significant difference in the spherulite morphology of the crystalline phase. The change in the crystal growing directions inside the spherulites due to the

presence of ABS may be a reason for the anomalous spherulite growing rate. However, this phenomenon remains unclear and is currently under investigation.

CONCLUSIONS

It was possible to ascertain in this study that blending ABS with PBT did not affect the melting process of the PBT crystalline phase. This is in agreement with the observed immiscible state for PBT/ABS blends through depression melting temperature and glass transition temperature shift criteria. On the other hand, PBT crystallization characteristics such as nucleation and spherulitic growth were markedly affected by the presence of ABS in the blends. The nucleation rate of the spherulite decreased due to the presence of ABS in the blends, whereas the spherulitic growth rate increased drastically. The change in nucleation behavior is attributed to diffusion barriers due to the increase in melt viscosity, whereas the increase in spherulite growth rate is attributed mainly to preferential directions for the lamellar crystal growth.

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