Thermal and Crystallization Properties of PBT/ABAS Blends

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ABSTRACT: Blends of poly(butylene terephthalate) (PBT) with poly(acrylonitrile-butyl acrylate-styrene) (ABAS) were characterized by differential scanning calorimetry, infrared, thermogravimetric analysis, and wide-angle X-ray diffraction (WAXD) studies. Addition of ABAS polymer to PBT improved the thermal stability of PBT. Infrared studies showed that ABAS polymer chemically interacts with PBT. The crystallization behavior of PBT was modified in the presence of ABAS polymer. The ABAS polymer showed inappreciable effect on melting behavior of PBT but decreased its crystallization. WAXD studies showed some modification in PBT peaks and a peak with increasing intensity corresponding to the β-crystalline form of PBT. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1657–1663, 2009

Key words: PBT/ABAS blends; thermal properties; FTIR; DSC; TGA; WAXD

INTRODUCTION

Transesterification or ester exchange reactions are well established in polyesters at melt processing temperatures above 230°C and are reported to bring about partial miscibility in certain PET-based blends.[1–3] These reactions, which have been studied by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimetry (DSC), lead to the formation of a copolymer at the interphase. These copolymers reduce the interfacial tension and enhance the miscibility and the phenomenon is broadly recognized in reactive processing.[4,5]

The polyester poly(butylene terephthalate) (PBT) is an engineering thermoplastic with excellent property profiles.[6,7] However, PBT lacks in notched impact strength. To enhance the impact strength and widen the applications of PBT, the polymer has been blended with other polymers, e.g., phenoxy resin,[8] poly(ethylene terephthalate)[9], polyarylate,[10] etc. These blends are reported to be miscible. Some partially miscible blends were also obtained with polycarbonate[11] and poly(ester carbonate)[12] polymers. Chemical reactions were shown to occur in these blends.

The terpolymer acrylonitrile–butyl acrylate-styrene (ABAS) possesses enhanced environmental and thermal resistance.[13] Thus, blends of PBT/ABAS may exhibit superior thermal oxidation and UV resistance for outdoor applications.

In this work, we studied the thermal and crystallization properties of PBT/ABAS blends at varying concentrations of the blending polymer ABAS. Thermal stability studies have been made by thermogravimetric analysis (TGA), whereas crystallization parameters have been evaluated from DSC and wide-angle X-ray diffraction (WAXD) measurements. These properties have been explained on the basis of chemical reactions between the component polymers of the blends.

EXPERIMENTAL

Materials

PBT (LUPOX-HV1010 of M_n = 25,000 and PDI = 2.2) was obtained from LG Chemicals, Seoul, South Korea.[14,15] The carboxylic acid content in PBT was 63 equiv/10^6 g (1.6 carboxylic acid units per chain based on the M_n).The blending polymer, ABAS, a product of Eliokem, Villejust, France, was a saturated, pre-crosslinked terpolymer of butyl acrylate, styrene and acrylonitrile with carboxylic end groups, and outstanding thermal and UV resistance.[13]

Blend preparation

PBT pellets and the ABAS powders were vacuum dried at 120°C[14] and 90°C,[13] respectively, for 3 h. The blends were made by mixing varying proportion of ABAS polymer (0–50 phr, 0.06–0.39 volume fraction, Φ_d) with PBT by first tumble blending and then by melt compounding in a corotating Twin Screw Extruder, model JSW J75E IV-P (L/D = 36, screw diameter D = 30 mm). The extruder compounder was

operated at 246 rpm and the temperature profiles varied from 195 to 245°C from the feed zone to the die zone. Extruded strands were chilled in cold water, palletized, and vacuum dried at 100°C for 4 h. These pellets were injection molded into dumbbell-shaped tensile specimens on an L&T-Demag injection molding machine (model PFY 40-LNC 4P).The barrel temperatures were 80–255°C from the feed zone to the die zone; the mold temperature was ambient at 30°C.

Measurements

Powder samples for DSC analysis were obtained by filing down tensile specimens. DSC analysis was carried out on a Perkin Elmer DSC7 instrument under continuous nitrogen flow in sealed aluminum pans. The Calorimeter was calibrated using an indium standard (melting temperature, $T_m = 156.4$ and heat of fusion, $\Delta H_f = 28.4$ J/g). The samples prepared from filing the injection molded specimens weighed 5 ± 1 mg. The cyclic heating and cooling scans were taken between 35 and 250°C with a heating and cooling rate of 10°C/min with an isothermal heating of 3 min at 250°C.The crystallinity(%) of PBT in the blends was calculated using 145.5 J/g as the melting enthalpy for 100% crystalline PBT.[16]

Powder samples were also used for the TGA studies performed on a DuPont 951 thermal analysis system in a dynamic atmosphere of oxygen free nitrogen from ambient temperature to 750°C at a heating rate of 10°C/min. The TGA curves were obtained from TGA traces as the residual mass (%) against temperature. From the curves, the parameters[17] T_{onset}, T_{max}, and T_f, were evaluated to characterize the thermal stability of the blends

ATR-FTIR spectra of PBT, ABAS polymer, and the blends were obtained on an IR 200-Thermonicolet instrument using films compression molded at 255°C and 10-ton pressure. A membrane sample was pressed against each side of a zinc selenide internal reflection element.

WAXD measurements were made using machined rectangular block samples 12 mm × 10 mm × 3 mm from tensile specimens to characterize the crystalline structure of the blends. The samples were scanned at 2θ range 10°–35° using scan speed = 0.05° and step size = 0.01° (scan rate of 3°/min) at ambient temperature on an X'Pert Pro PANanlytical model of X-ray diffractometer (40 kV, 30 mA) with Cu Kα radiation (β = 1.541 Å).

RESULTS AND DISCUSSION

In situ compatibilization

In polymer blends consisting of polyesters, in situ compatibilization is reported to take place through

reactions between —COOH and —OH end groups as well as ester exchange reactions between two polyesters.[18–20] The in situ graft copolymers formed tend to reside along the interphase and act as compatibilizers. The possible reactions of PBT end groups and ABAS polymer (Scheme 1)[21] bring about some miscibility. The acrylate group of ABAS copolymer can react readily with the PBT macromolecules, forming either ABAS/PBT graft copolymer or crosslinked ABAS/PBT.[21] Ester exchange reactions between ABAS and PBT as acrylate groups of ABAS molecules may also give rise to grafted polyester chains (Scheme 1).[21] These reactions are confirmed by IR studies. The spectra obtained from neat PBT, neat ABAS, and a representative PBT/ABAS blend are shown in Figure 1. Table I shows the vibration frequencies of neat PBT, ABAS, and the blend and characteristic assignments. Disappearance of —C≡N str peak at 2237 cm^{-1} and appearance of new band at 1115 cm^{-1} in the blend indicate the involvement of —C≡N group of acrylonitrile component and —COOH end group of PBT in imide formation and mixed ester formation due to transesterification, respectively (Scheme 1).[18,21] The effect of these reactions can be seen on thermal stability studies of the blends.

Thermogravimetric analysis[17]

The TGA and differential thermogravimetric (DTG) thermograms of PBT, ABAS, and PBT/ABAS blends are shown in Figures 2(a,b) and 3(a,b), respectively.
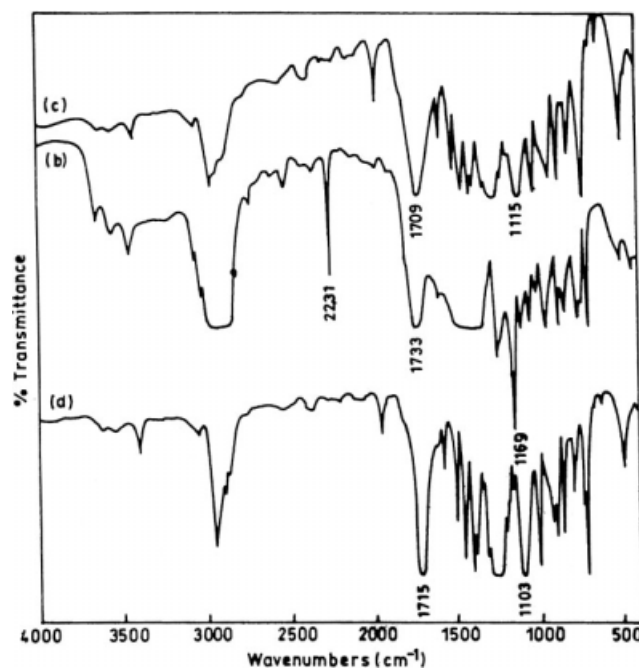

Figure 1 FTIR spectra of PBT (a), PBT/ABAS ($\Phi_d = 0.11$) blend (b), and ABAS polymer (c).

TABLE I
Characteristic IR Absorption Bands in PBT and ABAS Elastomer

Wave no. (cm^{-1})	Assignment
(a) PBT	
1,715	>C=O stretching
1,503	CH$_2$ bending of butylenes unit
1,348	CH$_2$ wagging
1,266	C—O—C asymmetric stretching
1,103	C—O—C symmetric stretching
1,018, 873, 727	Aromatic ring
810	C—H bending of terephthalic unit
(b) ABAS	
Acrylate constituent	
1,733	>C=O str of acrylate ester unit
1,169	C—O—C symmetric stretching
1,387	CH$_3$ symmetric deformation
1,456	CH$_3$ asymmetric deformation
Acrylonitrile constituent	
2,237	—C≡N stretching

Table II shows the T_{onset}, T_{max}, and T_f values of the neat polymers and the blends. Pure PBT and all the blends show single step decompositions. There is observable enhancement in thermal stability of the blends. T_{onset}, T_{max}, and T_f values are higher than those of the neat PBT matrix as well as the neat ABAS polymer. T_{onset} increases with ABAS content in the blend, at $\Phi_d = 0.39$ the T_{onset} is 20°C higher than that of PBT. T_{max} is enhanced on an average by 10°C up to this blend composition. T_f of PBT enhances with Φ_d showing a maximum at $\Phi_d = 0.2$; the value then decreases a little and levels off.

The increase in T_{onset} indicates an increase in thermal stability of the blends that can be attributed to the chemical interactions such as formation of imide linkages and transesterification that increase the average effective bond strength and/or the intermolecular attraction and thus stabilize the blends against thermal degradation. Chemical cross-links increase the number of bonds that must be broken before the material exhibits weight loss and sequential deterioration of important properties. Cross-linking thus increases the thermal stability. The occurrence of chemical reactions including an extent of cross-linking of PBT and ABAS (Scheme 1) were indicated by IR studies.

DSC studies

Figure 4 presents the DSC scans (first heating) of PBT and PBT/ABAS blends; scans for the second heating are shown in Figure 5. It can be observed from the first heating scans that there is no change in crystallization melting temperature of PBT; however, the enthalpy of melting decreases with increases in ABAS content, implying a decrease in the crystallization of PBT (Fig. 4). In the curves for

the second heating (Fig. 5), a minor melting peak appears that is a well-known feature of thermoplastic polyester crystallized in DSC measurements.[22–25] The origin of these peaks has been ascribed to the presence of different morphologies and simultaneous melting and reorganization of the crystallites.[26] However, the enthalpy of melting decreased with increase in ABAS content, which indicates that ABAS impairs the crystallinity of PBT. The normalized crystallinity, (X_c), decreased by $\sim$ 12% when ABAS volume fraction varied from 0 to 0.39 (Table III). This may be due to phase interactions between the two polymers, as indicated earlier.[21]

Various crystallization parameters were also determined from the DSC cooling scans[27] (Fig. 6) and are presented in Table IV. The description and
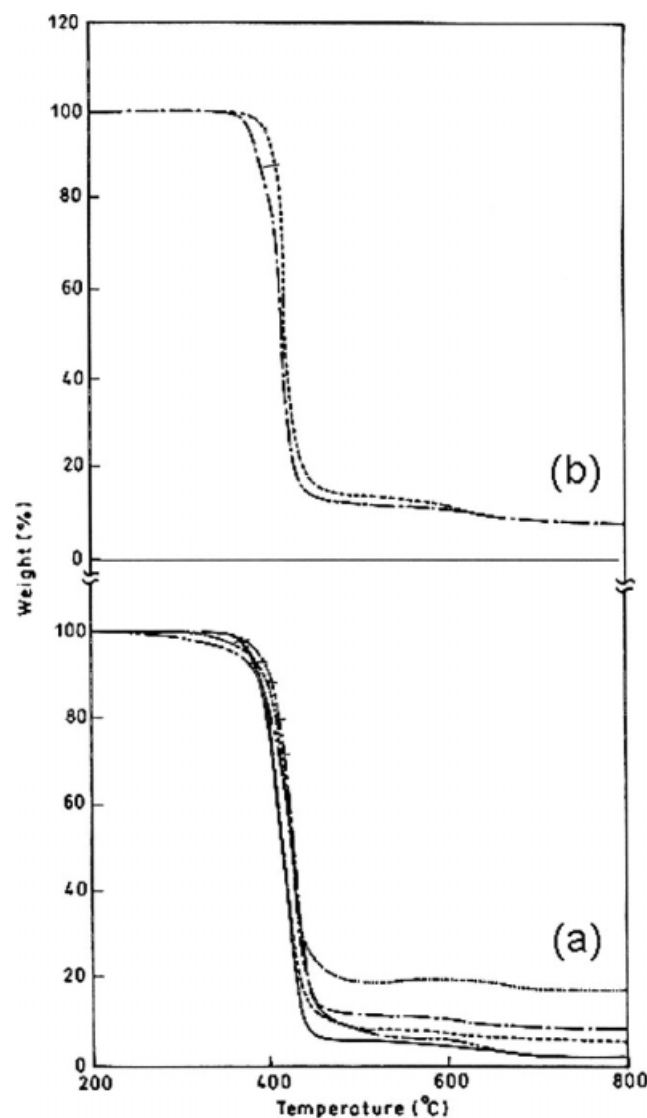

Figure 2 Experimental TGA scans for (a) PBT (—), ABAS (...) and PBT/ABAS blends at varying Φ_d: 0.06 (---); 0.20 (– – –); 0.39 (–··–), and (b) at $\Phi_d = 0.11$ (— - —); 0.31 (— - - —).
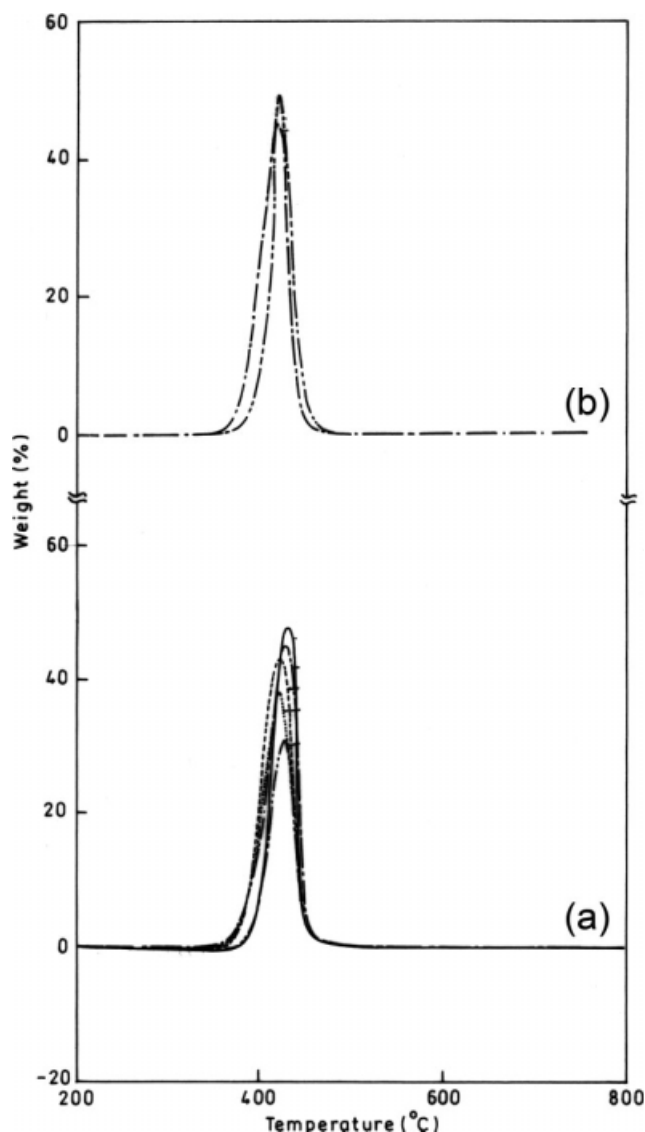
Figure 3 Experimental DTG scans for (a) PBT (—), ABAS (...) and PBT/ABAS blends at varying Φ_d: 0.06 (---); 0.20 (–––); 0.39 (–··–), and (b) at Φ_d = 0.11 (...); 0.31 (–·–).

significances of these parameters are described elsewhere.[27] The crystallization onset temperature, T_c, indicates the commencement of the crystallization process and is dependent on the nucleation rate. The peak temperature of the crystallization isotherm, T_p,

TABLE II
Values of TGA Parameters T_{onset}, T_{max}, and T_f in PBT, ABAS, and PBT/ABAS Blends

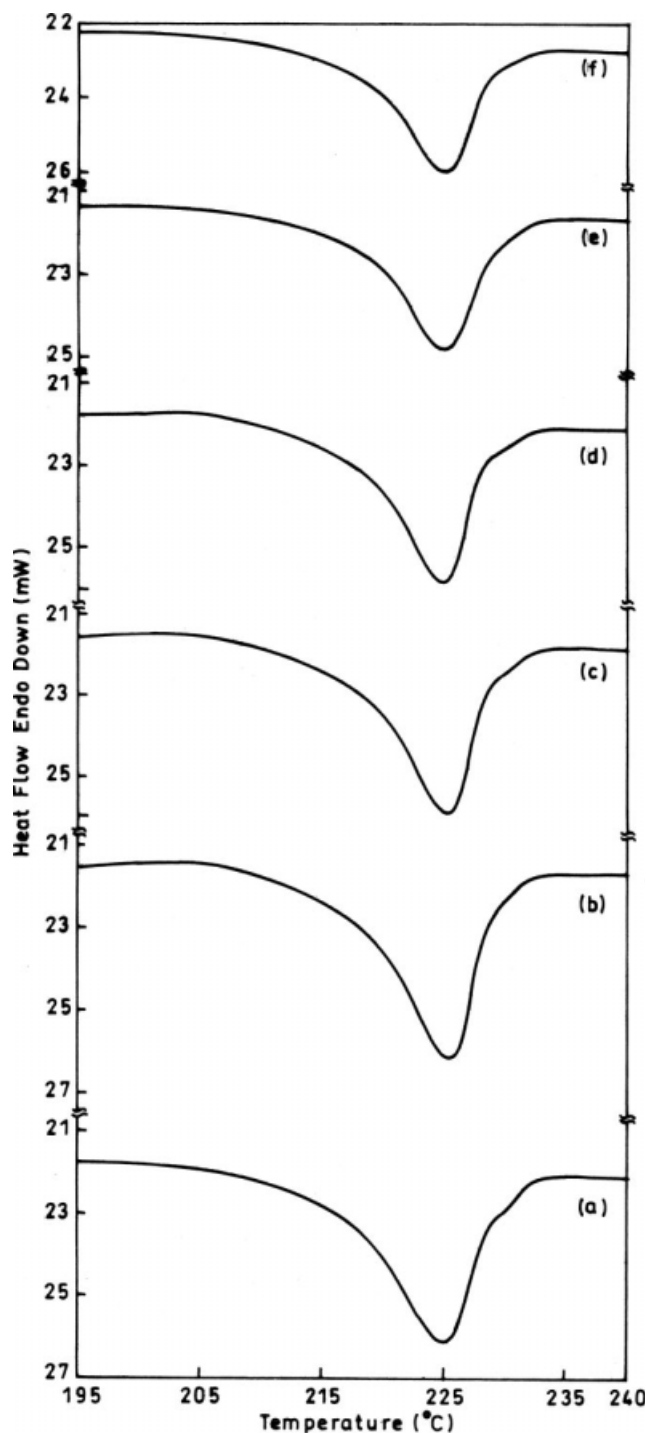| Φ_d	T_{onset} (°C)	T_{max} (°C)	T_f (°C)
0 (PBT)	394.3	419.1	434.8
0.06	395.6	420.2	441.9
0.11	398.7	419.1	442.1
0.20	404.3	424.9	444.5
0.31	408.7	429.0	439.9
0.39	414.2	429.6	440.2
1 (ABAS)	395.6	421.9	444.6

Figure 4 First heating DSC scans of PBT (a) and PBT/ABAS blends at varying Φ_d: 0.06 (b); 0.11 (c); 0.20 (d); 0.31 (e); and 0.39 (f).

is a function of the super cooling. Increase in T_p implies increase in the overall rate of crystallization of the polymer. The initial slope in the high-temperature side of the scan (measured as the tangent of the angle formed by the upward surge of the scan), S_i, indicates the rate of nucleation for crystallization; the higher the value, the higher the nucleation rate.
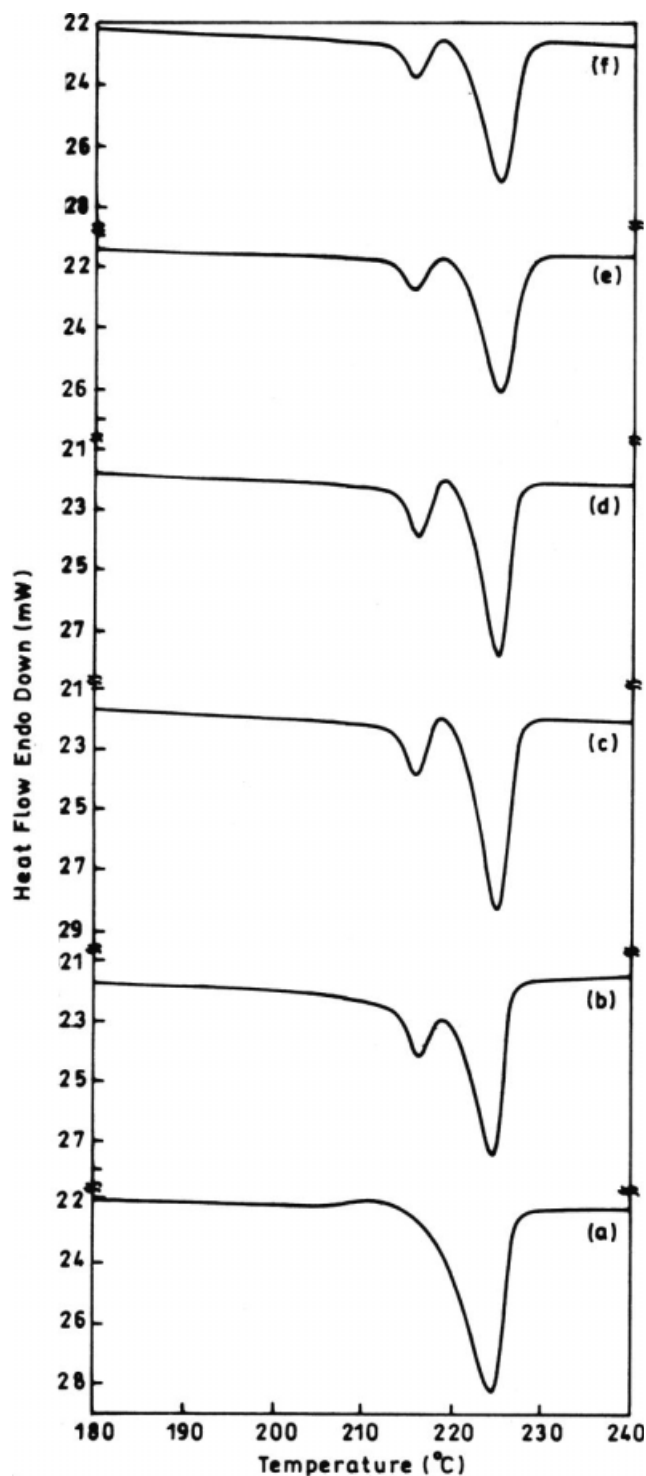
Figure 5 Second heating DSC scans of PBT (a) and PBT/ABAS blends at varying Φ_d: 0.06 (b); 0.11 (c); 0.20 (d); 0.31 (e); and 0.39 (f).

TABLE III
Values of DSC Crystallization Melting Temperature (T_m, ○C), Enthalpy of Crystal Melting (ΔH_f, J/g), and DSC and X-Ray Crystallinity (%) of PBT in PBT/ABAS Blends

	T_m (°C)		ΔH_f (J/g)		X_c (%)	
Φ	LMC[a]	HMC[b]	LMC	HMC	DSC	X-ray
0	–	224.5	–	45.7	31.4	38.6
0.06	216.0	225.1	3.8	40.2	27.6	34.8
0.11	215.8	224.9	5.61	30.5	27.1	27.9
0.20	215.6	224.7	5.38	29.5	25.9	27.2
0.31	215.3	224.9	3.47	26.2	21.9	21.9
0.39	215.4	224.9	3.69	20.9	19.3	19.5

[a] LMC, low melting crystals.
[b] HMC, high melting crystals.

measure of the degree of crystallinity. The quantity T_c–T_p is indicative of the rate of crystal growth; the smaller the value, the higher the rate of crystal growth.

It may be observed that the values of T_c, T_p, S_i, A/m, and ΔW decrease, whereas T_c–T_p increases with increase in ABAS content. The decrease in T_c indicates that the ABAS polymer delays the crystallization of PBT. Decrease in T_p indicates an increase in super cooling, which may indicate that the ABAS polymer enhances amorphization of PBT. The decrease in the value of S_i points toward a decrease in the nucleation rate of crystallization of PBT in the presence of the ABAS polymer. The increase in the values of T_c–T_p also indicates the retardation of the crystal growth of PBT by ABAS polymer. An overall effect of the extent of crystallization (A/m) of PBT decreases substantially in the presence of ABAS polymer. The extent of decrease in ΔW is an indication of narrower crystallite size distribution on

The width of the scan at half height (after normalizing the value by dividing by the mass of the crystallizable polymer), ΔW, is indicative of the crystal size distribution; the smaller the value, the narrower the distribution. The ratio of the scan area (A) to the mass (m) of the crystallizable component, A/m, is a
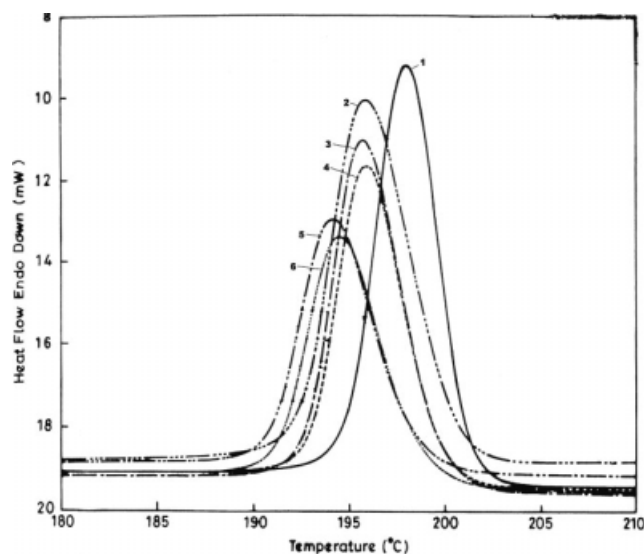

Figure 6 DSC cooling scans of PBT (1) and PBT/ABAS blends at varying blend composition, (Φ_d): 0.06 (2); 0.11 (3); 0.20 (4); 0.31 (5); and 0.39 (6).

TABLE IV
Values of DSC Crystallization Parameters of PBT in PBT/ABAS Blends

Φ_d	A/m (J/g)	T_c (°C)	T_p (°C)	S_i (arbitrary units)	ΔW (arbitrary units)	$T_c - T_p$ (°C)
0	49.5	202.0	198.2	80.0	2.9	3.8
0.06	44.3	201.8	196.2	70.0	2.3	5.6
0.11	41.6	200.0	195.8	70.1	2.5	4.2
0.20	38.8	200.0	195.9	70.1	2.4	4.1
0.31	34.1	199.5	194.4	69.0	2.7	5.1
0.39	30.8	199.0	194.4	65.0	2.7	4.6

account of delayed crystal nucleation and decreased crystal growth.

It may be inferred that PBT and ABAS is partially miscible through the formation of imide linkages and transesterification reactions[18,20] as well as an extent of cross-linking. Thus the mobility of PBT was hindered, which led to its decrease in crystallinity.[28] WAXD studies also supported this observation (next section). This decrease in the crystallinity of the major phase PBT also contributed to the decrease in the tensile strength and modulus and increase in the impact strength of the blends.[20] It may therefore be argued that the PBT/ABAS blends are essentially partially miscible materials with at least one PBT/ABAS mixed amorphous phase.

WAXD studies

Figure 7 shows X-ray diffractograms for PBT, ABAS, and PBT/ABAS blends. The intensity of diffraction peaks decreases as ABAS polymer increase in the blends. PBT samples have five strong peaks at $2\theta = 16.4°$, $17.7°$, $21.1°$, $23.8°$, and $25.4°$. It has been shown[29–31] that these peaks represent diffraction of the (011), (010), (111), (100), and (111) planes, respectively, whereas ABAS has no crystalline peak. PBT crystallizes in two crystalline modifications, α and β forms. The latter is formed due to mechanical deformation. The peak at $2\theta = 29.9°$ corresponds to β forms of crystals, which can be observed in the blends and the intensity of this peak increases with increase in concentration of ABAS. The β form is not expected in the present case as none of the samples studied are oriented. However, the results show transition of the α form to β form in the presence of ABAS polymer and the intensity of diffraction peaks decrease as ABAS polymer content increases in the blends. The positions of the diffractions remain unchanged in the blends compared with the pure PBT, which indicates that ABAS resin is not incorporated into the PBT crystals and does not change the PBT unit cell. However, the decrease in crystallinity and appearance of β form showed that there are some interaction between the PBT and ABAS polymer.

In neat PBT, the growth of crystallites is higher in the direction perpendicular to (100) plane. In the blend at $\Phi_d = 0.06$ the growth of crystallites is suppressed in almost all the directions and a new peak corresponding to ($\bar{1}11$) plane has been generated. Up to $\Phi_d = 0.20$ in the blend, there is an increase in crystalline growth in the direction perpendicular to (010), ($\bar{1}11$), and (100), whereas in ($\bar{1}11$), direction the crystal growth increases continuously up to $\Phi_d = 0.39$. In other directions, although the growth is
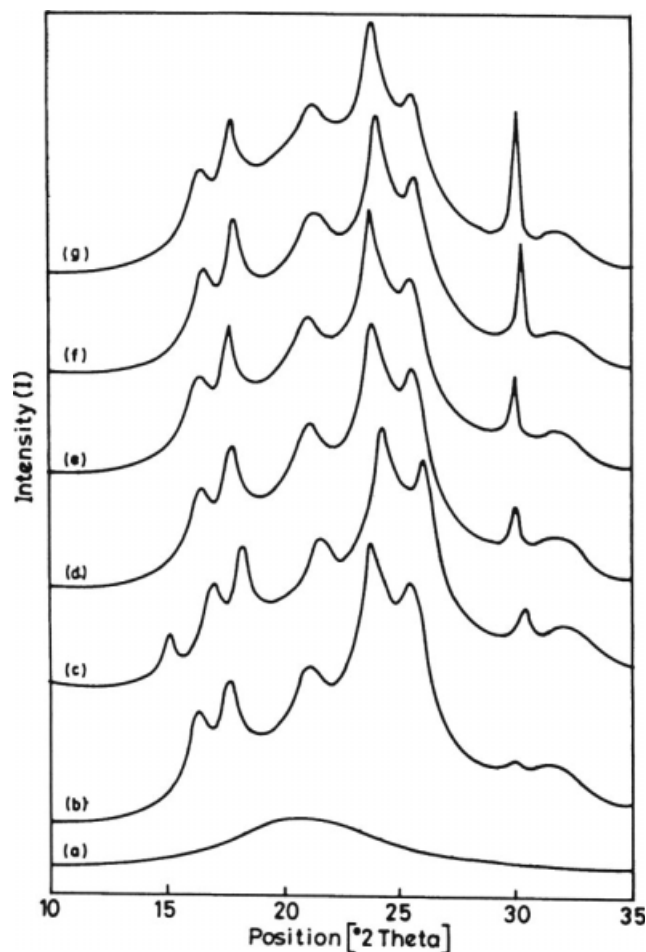

Figure 7 XRD profiles of ABAS (a); PBT (b) and PBT/ABAS blends at varying blend compositions (Φ_d): 0.06 (c); 0.11 (d); 0.20 (e); 0.31 (f); and 0.39 (g).

suppressed, the preferred direction of growth of crystallite is (100) plane.

The crystallinity (%) of PBT in the blends calculated following the procedure described elsewhere,[32,33] is shown in Table III. The parameter decreased with increase in ABAS concentration. Partial miscibility between the component polymers have been shown in the IR studies. We suspect that this interphase interaction causes an impediment in the mobility of the PBT chains, decreasing its crystallinity. The WAXD studies thus provide a supporting evidence of decrease in the crystallinity (%) of PBT observed in the DSC studies in this work.

CONCLUSIONS

PBT may be reactively compatibilized with ABAS polymer at melt blending conditions. This is the result of a transesterification reaction that leads to mechanically compatible hetrophase blends. In this work, significant evidence has been found to support the in situ compatibilization for PBT/ABAS blends. DSC and WAXD studies showed that crystallinity of PBT decreases with increase in ABAS polymer content due to the interphase interactions. Addition of ABAS to PBT improves the thermal stability of the blends.

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