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Phase Behavior of Poly(butylene terephthalate)/Polyarylate Blends

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ABSTRACT: In the present paper, we explore the amorphous phase behavior of poly(butylene terephthalate) (PBT)/polyarylate (PAr) blends, primarily using dielectric spectroscopy. Small-angle X-ray scattering experiments show clearly that the PAr resides in the interlamellar zones. We observe two dielectric relaxations associated with long-range motion for blends in which PBT has crystallized. Following from recent research on order–disorder interphases in crystalline blends, we tentatively assign the low-temperature transition to the presence of a crystal–amorphous interphase and the high-temperature relaxation to an unconstrained (mixed) amorphous phase.

Introduction

We have been interested recently in blends of two engineering polymers—poly(butylene terephthalate) (PBT) and a polyarylate (PAr) based on Bisphenol A and a 75/25 mole ratio of isophthalic and terephthalic acids. Our previous studies have focused on crystallization of PBT and PBT/PAr blends[1] and the influence of transesterification during melt processing on properties.[2] The present paper focuses on the amorphous phase behavior of untransesterified blends, particularly how this might be impacted by the existence of a crystal–amorphous interphase (e.g., refs 3 and 4).

Experimental Section

The PBT and PAr used were provided by Hoechst Celanese Corp. The PBT was of relatively high molecular weight; it had an intrinsic viscosity of 1.42 dL/g in a 40/60 wt % mixture of 1,1,2,2-tetrachloroethane (TCE) and phenol (Ph) at 30 °C, yielding[5] $\bar{M}_w = 83\,000$. The polyarylate had an intrinsic viscosity of 0.60 dL/g at 30 °C in tetrahydrofuran. This translates into $\bar{M}_v \sim 36\,000$.[6] Blends of PBT and PAr have been found to be miscible, both in the presence and absence of transesterification.[1,7] In the present study, in order to avoid transesterification, blends were prepared using the solution precipitation technique of Kimura et al.[7] The polymers were coprecipitated into methanol from a TCE/Ph solution (40/60 wt %) and refluxed several times with fresh methanol. The final product was dried under vacuum at a temperature in excess of the calculated blend T_g (taking into account PBT crystallinity).

Measurement of melting points (T_m) and heats of fusion was accomplished with a Perkin-Elmer differential scanning calorimeter, DSC-7. A heating rate of 20 °C/min was used in all cases, and the melting endotherm was defined by a base line constructed from 135 °C to a temperature above which no melting was observed. Degrees of crystallinity (W_c) were calculated using a perfect crystal heat of fusion for PBT of 34 cal/g.[8] All measured values reported are based on an average of a minimum of two DSC scans. Pure indium was used as the reference material to correct temperature values and heats of fusion.

Films for dielectric studies were prepared by hot pressing the solution-precipitated materials at 250 °C for ~5 min. Samples cooled rapidly from the pressing temperature to room temperature will be referred to as "as-prepared". Measurement of the dielectric constant and loss from –150 to –220 °C and 0.1–100 kHz was made using a Hewlett-Packard Model 4274A multifrequency LCR meter. A heating rate of 2 °C/min was used in all experiments. Samples that have been heated to 220 °C during the course of a dielectric run then cooled to room temperature will be referred to as "2nd run" samples. As will be seen, these samples are comparatively well-crystallized.

Small-angle X-ray scattering (SAXS) was conducted (on the well-crystallized (2nd run) samples only) using pinhole optics for collimation and a Rigaku Denki generator operated at 40 kV and 50 mA. The scattering intensity was collected on a Braun position-sensitive proportional counter and was Lorentz corrected (by multiplying the scattered intensity by s^2, where $s = 2 \sin \theta/\lambda$). Average thicknesses of the crystalline ($\langle d_c \rangle$) and amorphous ($\langle d_a \rangle$) regions were estimated either by using a correlation function analysis[9] or from the measured long period and degree of crystallinity. Values derived from either approach were very similar. Those derived from the correlation function analysis are reported here.

It is critically important to establish any detectable levels of transesterification in the blends particularly because of the nature of the relaxation behavior to be presented shortly. The most direct evidence is based on 500-MHz ^{1}H NMR experiments. In a previous paper,[2] we observed the occurrence of two distorted NMR doublets (associated with terephthalate protons) near 8.3–8.4 ppm after processing PBT/PAr blends under conditions that are more or less typical for melt blending. These doublets can be associated with unsymmetrical substitution around the terephthalate units (i.e., aliphatic–aromatic) and measurement of integrated intensities permits the degree of randomness and average sequence length of PBT units as a function of thermal history to be calculated. However, these peaks are absent in the blends as prepared in the present study. In addition, the PBT degree of crystallinity and melting point were found to decrease significantly upon melt processing. As will be described shortly, no such decrease in crystallinity was observed for the solution-precipitated blends and only a modest melting point depression, consistent with the miscible nature of this blend system, was found.

Results and Discussion

The results of our SAXS experiments are shown in Figure 1. The data here are for blends that have been well-crystallized; i.e., they have been heated slowly to 220 °C and then cooled to room temperature. The average long period (L) is seen to increase linearly upon dilution with PAr, while the crystal thickness is found to remain relatively constant. By difference we find that the amorphous layer thickness (which includes any interfacial boundary layer thickness) also increases linearly with PAr concentration. This leads to the conclusion that, similar to many other high molecular weight, crystalline miscible blends prepared under "usual" crystallization conditions,

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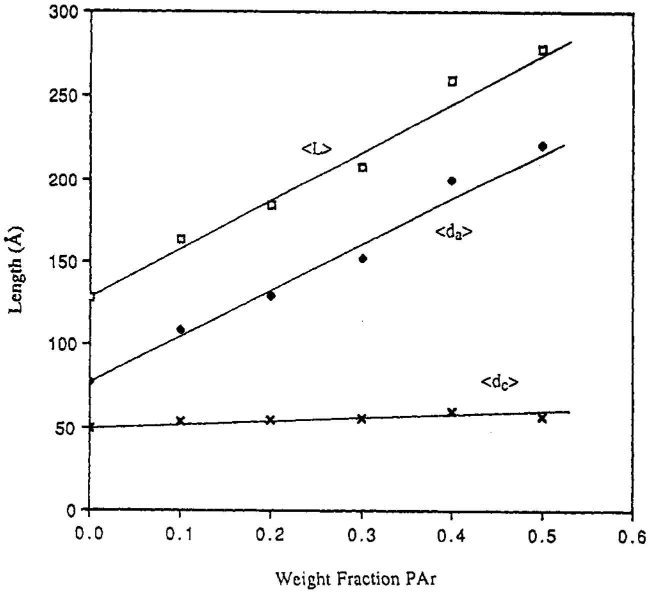

Figure 1. Average long period ($\langle L\rangle$) and crystalline ($\langle d_c\rangle$) and amorphous layer ($\langle d_a\rangle$) thicknesses derived from SAXS of the well-crystallized PBT/PAr blends.

the PAr resides in the interlamellar zones. Considering the crystallinity of these samples, the densities of the two polymers, and the SAXS data, *there is no evidence to suggest that significant PAr resides outside of the interlamellar regions.* The significance of this observation will be seen shortly.

The SAXS data for the well-crystallized samples is tabulated in Table I along with the results of DSC experiments on the same well-crystallized materials. As expected, the weight fraction crystallinity decreases as one adds more diluent, but based on the weight of PBT in the mixture, the crystallinity (W_c(PBT)) is found to remain constant up through 50% PAr. The experimental melting point was found to be depressed by a few degrees, consistent with the miscible nature of this blend. It should be noted that relatively large sample sizes were used to acquire the T_m's reported in Table I and this is the likely source of the apparent scatter in the reported values. Equilibrium melting points ($T_m°$) for PBT and selected PBT/PAr blends have been determined using the approach of Hoffman and Weeks[10] and with special consideration given to determining the "true" T_m of crystals formed at a given crystallization temperature.[11] Extrapolated $T_m°$'s for the blends and pure PBT were found to be the same within experimental error.[1]

The amorphous phase behavior of the PBT/PAr blends was investigated using dielectric spectroscopy. Figure 2 is a plot of the dielectric tan δ as a function temperature at a frequency of 2 kHz for PBT and a number of as-prepared blends. In this case, only PBT and three of the blends (90/10, 80/20, and 70/30 PBT/PAr) are crystalline. The degrees of crystallinity based on the weight of PBT in the blend are 37 (PBT), 32, 30, and 27%, respectively. The transition observed for PBT in Figure 2 is associated with cooperative, T_g-like motion (we will term this the β relaxation). As PAr is added, the relaxation shifts to higher temperatures and perhaps broadens somewhat. The relaxation for the amorphous 60PBT/40PAr blend actually moves to lower temperatures, presumably due to the higher PBT concentration in the amorphous phase as well as the loss of restrictions to chain mobility. The transition temperatures for the other blends move progressively to higher temperatures with increasing PAr content. Crystallization can be noted for a number of the originally amorphous blends above the transition temperature upon heating during the dielectric experiments. Finally, although not explicitly shown in Figure 2, relatively high conduction losses are observed at this frequency (and at the other frequencies which we probed) at temperatures above the transition temperature.

The relaxation behavior of the well-crystallized blends (Figure 3) is considerably different from that shown in Figure 2 and reminiscent of some recent work by us and others on crystal–amorphous interphases in such crystalline systems.[4,12–15] For weakly interacting miscible blends like poly(ethylene oxide) (PEO)/poly(methyl methacrylate) it has been found that, in addition to a mixed-phase transition (T_g), a relaxation persists at the same temperature as the pure crystalline component and decreases in intensity as the overall PEO crystallinity decreases.[4] This relaxation has been interpreted as arising from the order–disorder interphase, which was found to be pure PEO by Russell et al.[16] Such behavior has, in fact, been predicted using a lattice model by Kumar and Yoon.[3,17] In addition, these authors predict that the amorphous polymer can penetrate into the interphase of partial order if the interaction parameter (χ) is large and negative (i.e., strong interactions) and, perhaps, for blends containing stiff crystalline polymers.

The 10PBT/90PAr blend, whose relaxation behavior is depicted in Figure 3, is amorphous and exhibits a single relaxation at approximately the expected location. For the 70/30, 60/40, 50/50, and 30/70 blends we observe two transitions—one at low temperatures that decreases in intensity and shifts to higher temperatures with increasing PAr content and one at high temperature, in close proximity to the α-transition (T_g-like) for PAr. The transition for the 70/30 and 60/40 blends is obscured at 2 kHz due to the presence of significant dc loss but can be seen at higher frequencies. We believe that we should also observe high-temperature transitions for the 90/10 and 80/20 blends, but the highest frequency available was insufficient to allow us to reduce conduction losses at higher temperatures to an acceptable range and, in addition, the transition at higher temperatures is approaching or exceeding the melting point. It should be emphasized that, for example, when a 50/50 blend was cooled originally from the melt, it was amorphous and exhibited a single, intermediate relaxation associated with cooperative motion (see Figure 2). When crystallized by effectively annealing at a maximum temperature at 220 °C, we observe two distinct relaxations.

The compositions of the two phases associated with the observed loss maxima can be estimated in a straightforward manner.[18] To do so, we define w_{α_1} and w_{α_2} as the weight fractions of the lower and upper temperature relaxing phases, respectively. The weight fractions of the two polymer components of the blend are given by $\bar{w}_{ij}$ and w_{ij}. The former, barred notation represents the weight fraction of the ith component (1 = PBT, 2 = PAr) in the jth phase (1 = lower temperature phase, 2 = upper temperature phase) referred to 1 g of each phase. The various w_{ij} (unbarred) are the weight fractions referred to 1 g of the total sample. A simple series of algebraic equations can be constructed based on the relationships between the weight fractions defined above as well as the total weight fractions of the polymers *in the amorphous phase.*[18] The assumption that is required is that the various $\bar{w}_{ij}$ can be calculated from a specific mixing rule (we chose to use the Fox equation (eq 19)) from knowledge of the experimental transition temperatures. For example, Table II presents amorphous phase compositions calculated for the four well-

Table I
DSC and SAXS Results for Well-Crystallized ("2nd Run") Samples

	W_c (%)	W_c(PBT) (%)	T_m (°C)	L (Å)	$\langle d_a \rangle$ (Å)	$\langle d_c \rangle$ (Å)
PBT	47	47	227.5	128	78	50
90PBT/10PAr	42	47	226.5	163	109	54
80PBT/20PAr	37	46	226.3	184	129	55
70PBT/30PAr	33	47	225.5	208	152	56
60PBT/40PAr	29	48	226.5	260	200	60
50PBT/50PAr	24	48	225.1	278	221	57
30PBT/70PAr	11	37	218.0/226.0			

Table II
Amorphous Phase Compositions for Poly(butylene terephthalate)/Polyarylate Blends

					wt fractions[a]							
overall composn	T_{α_1}	T_{α_2}	w_{α_1}	w_{α_2}	$\bar{w}_{11}$	$\bar{w}_{21}$	$\bar{w}_{12}$	$\bar{w}_{22}$	w_{11}	w_{21}	w_{12}	w_{22}
70PBT/30PAr	96[b]	214[b]	0.64	0.36	0.83	0.17	0.05	0.95	0.53	0.11	0.03	0.34
60PBT/40PAr	99[b]	208[b]	0.50	0.50	0.80	0.20	0.08	0.92	0.40	0.10	0.04	0.46
50PBT/50PAr	100[c]	196[c]	0.52	0.48	0.62	0.38	0.06	0.94	0.32	0.20	0.03	0.45
30PBT/70PAr	100[c]	204[c]	0.32	0.68	0.62	0.38	0.02	0.98	0.20	0.12	0.01	0.67

[a] For *i*, 1 = PBT and 2 = PAr. For *j*, 1 = lower temperature phase and 2 = upper temperature phase. [b] At 40 kHz. [c] At 2 kHz.

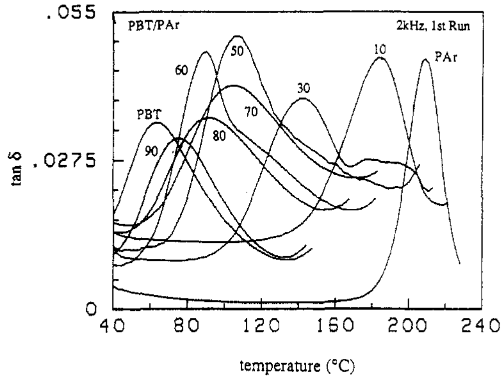

Figure 2. Dielectric tan δ vs temperature for as-prepared PBT, PAr, and selected blends at 2 kHz.

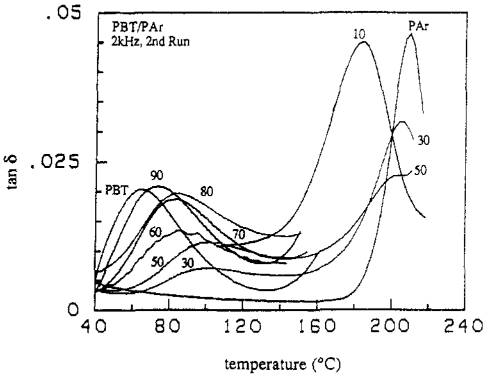

Figure 3. tan δ vs temperature for "2nd run" (well-crystallized) PBT, PAr, and selected blends at 2 kHz.

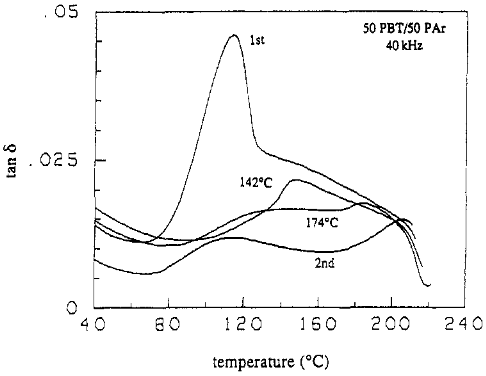

Figure 4. tan δ vs temperature (at 40 kHz) for 50/50 PBT/PAr blends: (a) as-prepared ("1st"); (b) annealed at 142 °C for 24 h; (c) annealed at 174 °C for 24 h; (d) "2nd run" sample (well-crystallized).

crystallized (2nd run) blends whose relaxation behavior is depicted in Figure 3. The calculations essentially substantiate the qualitative observations of the loss curves; that is, the high-temperature relaxing phase is predominantly PAr (90+%) and it increases in amount as more PAr is added to the blend. The low-temperature relaxing phase correspondingly decreases in amount, and the PBT concentration within this phase decreases from about 80 to 60% with increasing diluent concentration.

Finally we have conducted a series of annealing experiments which suggests strongly that crystallization leads to this relaxation behavior, not phase separation due to passing through a lower or upper critical solution temperature. Figure 4 contains the relaxation behavior (at 40 kHz) of several 50/50 blends with different thermal histories. The curve labeled "1st" is the behavior of the as-prepared blend, which as noted previously, is amorphous at room temperature. A single transition located near 110 °C (at this frequency) is noted. As before, crystallization is noted upon heating above this temperature. Two of the amorphous as-prepared blends were annealed at 142 and 174 °C for 24 h, respectively (W_c(PBT) = 38 and 46%, respectively). For the sample annealed at 142 °C it is difficult to tell if there is an additional relaxation at high temperature, due to the onset of PBT melting. In any event, the overall temperature shift and change in intensity of the "main" transition is consistent with depletion of PBT from the amorphous phase due to crystallization. As seen in Figure 4 annealing at 174 °C produces two clear relaxations. For a 2nd run 50/50 blend (which has a degree of crystallinity similar to that of the one annealed at 174 °C and has seen a maximum temperature of 220 °C), two relaxations are again noted, but they have moved to lower and higher temperatures, respectively. If this behavior were associated with passing through an LCST, heating to, for example, 230 °C would be expected to result in a blend with relaxation behavior similar to that of the 2nd run sample, whose transitions are perhaps even more widely separated. However, when the relaxation behavior of such a specimen is examined experimentally, it appears similar to that of the as-prepared (1st) material (although the data are somewhat complicated by crystallization during the dielectric measurement). This is presumably due to the fact that 230 °C is above the PBT melting point and the specimen remains amorphous upon cooling to room temperature. In fact, as noted earlier, the as-prepared samples have been exposed to 250 °C. In addition, the behavior seen in Figure 4 is apparently not associated with a UCST phenomenon. The conclusion is then that these multiple transitions are associated with different environments produced as a result of crystallization. Considering the experimental data available to date and the previous research noted above, we tentatively assign the high-temperature transition to that of the unconstrained ("mixed") amorphous phase and the low-temperature relaxation to the order–disorder interphase. In view of ref 3, the movement in the location of this lower temperature transition implies penetration of the PAr into the region of partial order. Research is continuing to further understand the origin of these relaxations.

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