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Melting Point Depression in Poly(butylene terephthalate)/Polyarylate Blends

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ABSTRACT: Poly(butylene terephthalate)/polyarylate (PBT/PAr) blends were prepared from phenol-TCE solutions coprecipitated into methanol. Blend powder was compression molded into thin sheets which were quenched in ice water. PBT/PAr blends have been shown to be miscible at all compositions in the melt or in the amorphous state. Homopolymer PAr is completely noncrystalline, while homopolymer PBT is semicrystalline. Differential scanning calorimetry (DSC) has been used to measure the melting behavior for PBT homopolymer and for 80/20, 60/40, 40/60, and 20/80 PBT/PAr blends. The thermodynamic melting points for PBT and blends, obtained by using Hoffman-Weeks plots, range from 249 °C for PBT homopolymer to 232 °C for 20/80, indicating a total 17 °C melting point depression. This is the first report of the melting point depression for PBT/PAr blends. Using the Nishi-Wang equation, we derived the Flory interaction parameter, χ , between PBT and PAr. Results show that the χ parameter depends on the blend composition, and it ranges from -0.65 for 80/20 to -0.22 for 20/80.

Poly(butylene terephthalate) (PBT) is one member of the family of polyesters used for such engineering applications as the matrix polymer in glass fiber reinforced composites. PBT is readily crystallizable and offers several processing advantages over its chemical relative, poly(ethylene terephthalate) (PET). The differential scanning calorimetric (DSC) upper melting temperature of PBT is about 230 °C,¹ lower than that of PET, which is near 270 °C,¹ making PBT processable at lower molding temperatures.

PBT has been shown to be able to be blended with other polymers such as polycarbonate and polyarylate (PAr).²⁻⁶ We are especially interested in the PBT/PAr blends, which have been shown to be miscible for all blend compositions in the melt and in the glassy amorphous state.⁴⁻⁶ It has been suggested previously that the melting point of PBT in the PBT/PAr blends is the same as that of pure PBT homopolymer,^{4,5} though no detailed study of this system had been presented. As described by Nishi and Wang,⁷ this suggestion of constant PBT melting point would lead us to conclude that the Flory interaction parameter χ is zero. However, this seems to be contradictory to the observed miscibility of the blends, which would imply a negative χ parameter. Crystal nucleation and growth kinetics are both very strongly dependent upon the degree of undercooling of the melt from the infinite crystal melting point. Therefore, it is of paramount importance to determine the effect of composition on the melting behavior in PBT/PAr blends because the degree of undercooling will affect the subsequent crystal morphology. It is the purpose of this brief report to present our study of the melting behavior of PBT/PAr blends, from which we have determined for the first time the melting point depression of the thermodynamic melting point. The thermodynamic, or infinite crystal, melting point depends on blend composition and decreases as PAr content increases. We find that the Flory interaction parameter is negative for all PBT/PAr compositions we tested.

Poly(butylene terephthalate) was obtained from Poly-science. PAr was obtained from Amoco, with a 1:1 ratio of isophthalic and terephthalic units. Blends of PBT/PAr weight fractions 80/20, 60/40, 40/60, and 20/80 were made by following the method of Kimura et al.,⁴ which involves coprecipitation from phenol/TCE into methanol.

The quenched samples were made by heating the pre-cipitates to 250 °C, holding for 60-90 s, compression molding, and then quenching in ice water. The quenched PBT and 80/20 blend are paracrystalline, while quenched 60/40, 40/60, and 20/80 blends are purely amorphous from the standpoint of wide-angle X-ray scattering. Melt-crystallized samples were prepared by heating the quenched amorphous film from room temperature to 250 °C for 1 min using a Mettler FP80 hot stage, then cooling quickly to the crystallization temperature T_c , and holding there for a time sufficient for completion of crystallization as required by the crystallization kinetics.⁵ No evidence of transesterification was found from NMR studies for the samples we prepared in the above way. Furthermore, we used differential scanning calorimetry (DSC) to test the transesterification reaction at 250 °C. We scanned the 60/40 blend at 20 °C/min from room temperature to 250 °C, held there for a certain time ranging from 2 to 30 min, cooled quickly to room temperature, and then scanned again to 250 °C. This cycling procedure was repeated more than 10 times. The DSC scans show no difference for accumulated times (at 250 °C) shorter than 10 min but show significant difference as the accumulated time approaches 1 h. This indicates that the blend sample we prepared for 1 min at 250 °C has not undergone any transesterification reaction. It is also consistent with the previous report by Kimura et al., indicating that transesterification reaction is severe only after holding at 250 °C for more than 100 min.⁴

The melting points and the endothermic heats of fusion were measured using a Perkin-Elmer DSC-4. We have previously investigated the effects of sample mass on the thermal response of our DSC for other polymers⁸ and found that for a factor of 8 difference in mass (0.8-6.5 mg) there was no difference in peak melting temperature. Therefore, we selected sample weights around 5 mg to achieve sufficiently precise heat of fusion and melting point measurements. The precision of the sample weight was within 0.01 mg. Indium was used as the temperature calibrator. The heat of fusion of PBT perfect crystal is 140 J/g.⁹

The DSC melting behavior for both cold and melt-crystallized homopolymer PBT has been studied previously.¹⁰⁻¹³ Multiple melting peaks have been found for

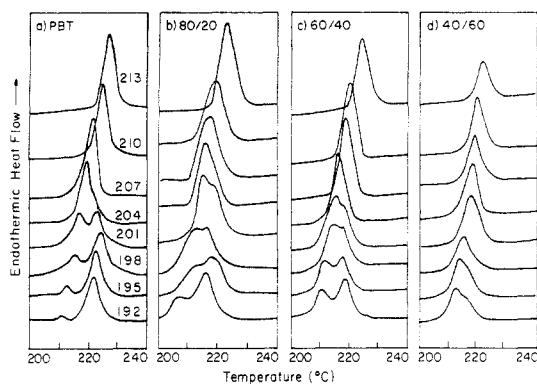


Figure 1. DSC scans at 20 °C/min of PBT and 80/20, 60/40, and 40/60 PBT/PAr blends, melt crystallized from 192 to 213 °C.

both cold and melt-crystallized PBT.^{10–13} In Figure 1a–d, we present the DSC thermographs for the melt-crystallized PBT and PBT/PAr blends 80/20, 60/40, and 40/60. Eight thermographs representing eight T_c 's are shown, displaced vertically by an arbitrary amount for clarity. The y-axis heat flow is normalized per unit sample mass. The scale is the same for Figure 1b–d, while the scale in Figure 1a is reduced by a factor of 2. The melt crystallization temperatures were chosen to range from 192 to 216 °C to ensure that there is no possible crystallization occurring during cooling from the melt to T_c . In all cases the samples equilibrated at T_c prior to the initiation of crystallization. A systematic change is observed in the melting behavior of PBT crystallized at different temperatures, as shown in Figure 1a. For T_c from 192 to 201 °C, we observe two melting peaks. The first peak, or lower temperature peak, increases in intensity as T_c increases, while the second, or higher temperature peak, decreases in intensity. At $T_c = 204$ °C, the two melting peaks merge into one broad peak, though there still exists a higher temperature shoulder. When T_c increases above 207 °C, only one single melting peak can be observed, which shifts to higher temperature as T_c increases to higher temperature. At these high crystallization temperatures, we did not observe the triple endothermic response which had been reported in other studies at lower crystallization temperatures.^{10–12}

In comparison to PBT, in Figure 1b–d we show the melting behavior of 80/20, 60/40, and 40/60 melt-crystallized blends for the same range of T_c . Blend 20/80 is omitted for the sake of brevity. Similar thermal features are observed for the PBT/PAr blends as compared with PBT homopolymer. For 80/20 and 60/40 blends, for T_c lower than 198 °C, we observe two melting peaks, the first of which increases and the second decreases in intensity as T_c increases from 192 to 198 °C. At T_c about 204 °C, the two melting peaks merge together, forming one single broad peak similar to the behavior of homopolymer PBT. For T_c higher than 204 °C, we only observe a single peak for both 80/20 and 60/40 blends, which shifts to higher temperature as T_c increases above 204 °C. For 40/60 blend, even at the lowest temperature (192 °C) as shown in Figure 1d, we observe a merging of the peaks, indicated by the presence of a higher temperature shoulder. Above 195 °C, we only observe a single melting peak, whose peak position increases from 213 to 223 °C as T_c increases from 195 to 213 °C.

The dual melting behavior of melt-crystallized polymer shown in Figure 1a–d is usually interpreted in terms of preexisting morphology and/or of reorganization, which has been discussed extensively before for PBT^{10–13} and for other polymers.^{14–16} In the case of melt crystallization at low undercooling, the lower temperature melting peak

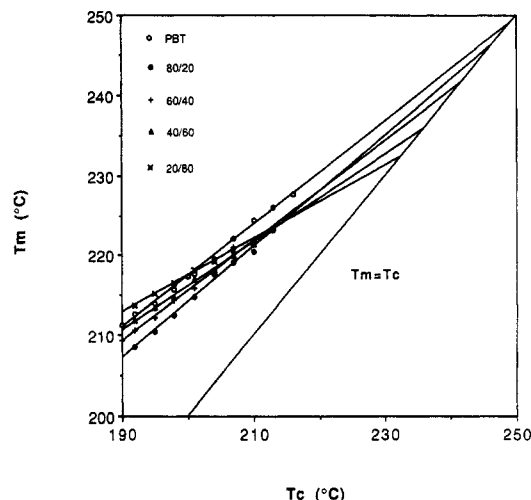


Figure 2. Hoffman-Weeks¹⁷ plot of the first melting peak temperature as a function of T_c for PBT and all blends.

Table I. Equilibrium Melting Point, Crystal Thickening, and Flory Interaction Parameters

sample	T_m (°C)	γ	χ_{12}
PBT	249.1 ± 1	1.55 ± 0.02	^a
80/20	246.0 ± 1	1.44 ± 0.02	−0.65 ± 0.2
60/40	241.6 ± 1	1.60 ± 0.02	−0.40 ± 0.05
40/60	235.9 ± 1	1.82 ± 0.05	−0.31 ± 0.02
20/80	232.4 ± 1	2.17 ± 0.07	−0.22 ± 0.01

^a Not applicable.

has usually been associated with the dominant lamellar population formed at T_c .^{14–16} Here, we present in Figure 2 the Hoffman-Weeks plot of the first melting peak temperature as a function of T_c for PBT and all blends. The Hoffman-Weeks equation is used to extrapolate the thermodynamic melting point according to¹⁷

$$T_m' = T_m(1 - 1/\gamma) + T_c/\gamma \quad (1)$$

where T_m' and T_m are the experimental (DSC) melting temperature and equilibrium melting temperature of PBT in the blends, respectively. For homopolymer PBT, the thermodynamic melting point, T_m° , would replace T_m in eq 1. γ is a proportionality factor between the initial thickness of a chain-folded lamella, l_g^* , and final lamellar thickness, l_c . In deriving eq 1, a very small δl has been assumed according to the theory of Hoffman et al. for secondary nucleation and crystal growth.¹⁸ This assumption can only be justified if the crystal thickening process takes places during crystallization, indicating γ is larger than unity for all blends.

By plotting the melting temperature of samples crystallized at different temperatures against T_c , eq 1 allows us to extrapolate to T_m , the thermodynamic melting point corresponding to fully chain extended crystals. The statistical scatter in the data for T_m vs T_c is generally small. For 20/80 and 40/60, all data points lie within ± 0.3 degrees of the line of best fit. For 60/40 and 80/20, one or two data points out of nine lie outside ± 0.3 degrees of the line of best fit. The most liberal error estimate of ± 1 degree has been used for all reported T_m values. The extrapolated T_m° for PBT homopolymer (open circles) is 249 °C, which is higher than the previous published results of Kimura et al.⁴ (240 °C), Runt et al.⁵ (236 °C), and Cheng et al.¹³ (245 °C). The factor γ and the extrapolated equilibrium melting temperatures of the blends are listed in Table I. The extrapolated values of T_m for PBT in the blends are lower than the equilibrium melting point of homopolymer PBT. Even with the most liberal error

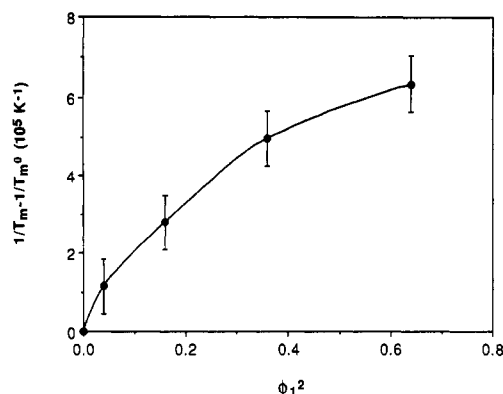


Figure 3. $1/T_m - 1/T_m^0$ vs square of PAr mass fraction.

estimates, the melting points of the blends are systematically depressed from PBT homopolymer.

The thermodynamic melting point, T_m , of the blends decreases as the PAr composition increases from 249 °C (for PBT/PAr 100/0) to 232 °C (for PBT/PAr 20/80). This is the first report of the observation of melting point depression in this system. The parameter γ ranges from 1.4 for 80/20 blend to 2.2 for 20/80 blend, indicating a significant crystal thickening from the initial nucleation stage during the crystallization at T_c . This thickening is therefore consistent with the assumption, and confirms the validity of using eq 1, as described previously by Rim and Runt.¹⁹

Melting point temperature depression has been found for other miscible polymer blends, such as PVF₂/PMMA⁷ and PEO/PVAL.²⁰ Thermodynamics predicts that the chemical potential of the crystallizable polymer is decreased due to the presence of the miscible amorphous polymer, resulting in a decrease in the melting point. This has been modeled by Nishi and Wang⁷ according to the following relationship:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_f V_1} \chi \phi_1^2 \quad (2)$$

where T_m and T_m^0 are the thermodynamic melting points of PBT in the blends and in the PBT homopolymer, respectively. R is the gas constant (8.34 J/K·mol), ΔH_f is the heat of fusion per mole of crystalline repeat units (9.20×10^3 J/mol-monomer), V_1 (266.2 cm³/mol-monomer) and V_2 (129.2 cm³/mol-monomer) are the volumes of the amorphous and crystallizable polymer repeat units, and ϕ_1 is the mass fraction of noncrystallizable polymer (PAr fraction in our case). We neglect the entropy contribution of mixing due to the high molecular weight nature of the polymers.⁷ Here, we apply the Nishi-Wang equation to obtain the interaction parameter χ for PBT and PAr. We plot $(1/T_m - 1/T_m^0)$ vs ϕ_1^2 in Figure 3. A nonlinear relation is observed, indicating that the χ parameter is dependent on the blend composition. The χ parameter can be computed from eq 1 for each blend composition and is also listed in Table I. Uncertainties in the values of V_2 , V_1 , and ΔH_f will affect the accuracy of the value of χ .²¹ Experimentally, the accuracy of χ depends upon the uncertainties in the extrapolated values of the equilibrium melting points. Using values of T_m and T_m^0 , we determine the error limits on χ which are reported in Table I. The χ parameter increases from -0.65 for 80/20 blend to -0.22 for 20/80 blend.

The melting point depression of PBT in the PAr blends we observed here has not been reported in previous studies of this system.^{4,5} Kimura and Porter reported no melting point depression for PBT/PAr blends.⁴ Therefore, the

interaction parameter was assumed equal to zero. But, Kimura et al. did not compare the equilibrium melting point of blends. Instead, they made the above conclusion based on a comparison of the experimental DSC melting points of the blend samples. Rim and Runt showed that using the DSC melting point will give an underestimate of the melting point depression, and therefore the χ parameter may be incorrectly assumed to be nearer to zero when the DSC melting point is compared.¹⁹

As shown in Figure 2, because of the different slopes among the blends, there is a crossover in the melting point data leading to the observation that the experimental melting points of some blends are even higher than the melting point of PBT homopolymer crystallized at the same T_c . This elevation of experimental melting point occurs for the samples crystallized at relatively lower temperatures, in the range 192–200 °C. Simply from eq 1, we would interpret the blend melting point crossover to be a reflection of different thickening factors among the blends. We offer the following as a possible explanation for the crossover. We have explored the nature of the PAr placement in these blends²² and found that there is nearly interlamellar placement of the PAr in the 80/20 blend, in agreement with previous work.⁶ The strong Flory interaction parameter for this blend, coupled with interlamellar placement of PAr, may lead to an inability of the PBT crystals to thicken easily. This would cause the thickening to be reduced in 80/20, giving this blend the highest slope among the blends. On the other hand, at very low PAr composition (20/80 for example), we find a noninterlamellar placement for the PAr.²² At low PAr content, PBT crystals may thicken more readily due to the reduction of PAr near the crystal surfaces. Runt et al.²³ suggest that experimental melting point elevation of blends compared to homopolymer may be due to changes in fold surface free energy, to crystal thickening, or to crystallite perfection changes upon blending. Clearly, this is an area requiring further study to separate these possibilities.

The depression of the thermodynamic melting point and the conclusion of a negative Flory interaction parameter for PBT/PAr blends are in agreement with the observed miscibility of this system. In a subsequent report, we describe the implications of the melting point depression on the phase behavior of these blends.²²

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