Miscibility and Melting Behavior of Poly(ethylene terephthalate)/Poly(trimethylene terephthalate) Blends

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ABSTRACT: The miscibility and melting behavior of binary crystalline blends of poly(ethylene terephthalate) (PET)/poly(trimethylene terephthalate) (PTT) have been investigated with differential scanning calorimetry and scanning electron microscope. The blends exhibit a single composition-dependent glass transition temperature (T_g) and the measured T_g fit well with the predicted T_g value by the Fox equation and Gordon-Taylor equation. In addition to that, a single composition-dependent cold crystallization temperature (T_{cc}) value can be observed and it decreases nearly linearly with the low T_g component, PTT, which can also be taken as a valid supportive evidence for miscibility. The SEM graphs showed complete homogeneity in the fractured surfaces of the quenched PET/PTT

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) has been recently introduced as a commercial polymer, joining the other linear aromatic polyesters, poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT). It is well known that PET and PBT are semicrystalline polymers with satisfactory thermal stability and mechanical properties, which have been widely used as fibers, bottles, packages, etc.¹ PTT is also a semicrystalline and aromatic polyester that made by the polycondensation of 1,3-propanediol (PDO) and terephthalic acid (TPA). Because of the different number of methylene group along the backbone of these polyesters, the chain flexibility of PTT is higher than that of PET, but lower than that of PBT. It combines the desirable physical properties

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blends, which provided morphology evidence of a total miscibility of PET/PTT blend in amorphous state at all compositions. The polymer-polymer interaction parameter, χ_{12} , calculated from equilibrium melting temperature depression of the PET component was -0.1634, revealing miscibility of PET/PTT blends in the melting state. The melting crystallization temperature (T_{mc}) of the blends decreased with an increase of the minor component and the 50/50 sample showed the lowest $T_{\rm mc}$ value, which is also related to its miscible nature in the melting state. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 431-437, 2008

Key words: polyesters; blends; miscibility; DSC; melting point

of PET (strength, stiffness, toughness, and heat resistance) with the processing advantages of PBT (low melt and mold temperatures, rapid crystallization, and faster cycles), while retaining basic polyester benefits of dimensional stability, electrical insulation, and chemical resistance.² These characteristics make PTT suitable for uses in fibers, films, packing, and engineering thermoplastic markets.²

Polymer blending is one of the most effective techniques to develop new materials with properties better than those of the original polymers. Blends of PET and PBT have been more widely studied because of their commercial importance.3-10 For PET/PBT blends, a single glass transition varying in composition was observed, and suggested that the components of PET and PBT were miscible in the amorphous phase.^{3,4} It was reported that both components crystallize simultaneously and each component forms its own crystal phase.3,4 Yishan and Kyung-Ju⁵ reported that the behavior of crystallization of PET/PBT blends from glassy state was influenced by entanglement and transesterification of chains. It was also shown that a small amount of PBT has significant effect on increasing the crystallization rate of PET in their block polymers.⁶ Mishra and Deopura investigated the crystallization behavior

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of PET/PBT blends at low percentage of the second component.⁷ It was found that the melting behavior of the isothermally crystallized sample shows that the crystallization behavior in the blend is governed by the mobility of PBT. The nonisothermal crystallization behavior shows that the crystallization process is hindered when the PBT content in the blend is less or higher than 6 wt %. Font et al. prepared PET/PBT blends by a ball milling technique; they found that PBT greatly influences the crystallization of amorphized PET by milling.⁸

PET is a slow crystallizing material,⁹ but PTT can crystallize easily without the presence of any nucleating agent.¹⁰ Therefore, it is also expected that blending of PET and PTT will offer an interesting route to combine the complementary properties of both polymers. PET/PTT blends were found to be fully miscible in amorphous state in accordance with criteria of microscopy morphology and thermal transition.^{11,12} Tae et al. investigated the ester-interchange reaction of PET/PTT blends and found the reaction increases homogeneity of the blends and decreases the degree of crystallinity of the melt blends.¹³ Jeon et al. found the tensile modulus and tensile strength of PTT/PET blends can be increased by introducing PET to PTT.¹⁴ The dyeing properties of PTT/PET blends have also been reported.¹⁵

The purpose of this article is to investigate the nature of miscibility and melting behavior in PET/PTT blends. Differential scanning calorimetry (DSC) and scanning electron microscope (SEM) were employed to study the miscibility and melting properties of the blends. The polymer–polymer interaction parameter χ_{12} and interaction energy density *B* were calculated from the equilibrium melting depression of PET using the Nishi-Wang equation.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (PET) in pellet form was kindly supplied by Shanghai Petrochemical Co. (Shanghai, China). Its intrinsic viscosity (IV) is 0.76 dL/g measured in a 60 : 40 wt % solvent of phenol and 1,1,2,2-tetrachloroethane at 30°C. Poly(trimethylene terephthalate) (PTT) (Corterra CP509201, Shell Chemicals, Montreal, Canada) in pellet form with an IV of 0.92 dL/g was used in this study.

Samples preparation

Before blending, both polymers were dried at 150°C for 5 h in an air oven to remove moisture in order to minimize the possibility of hydrolysis. The samples of PET/PTT blends, with compositions ranging from 90/10 to 10/90 in weight ratio, were prepared in a

30 mm co-rotating twin screw extruder (TE-34, Nanjing, China) with an L/D of 28, a barrel temperature ranging from 235° C to 280° C, and a screw speed of 40 rpm. The strand from the extruder was quenched in a water bath and cut into chips.

Characterizations

The measurement of the thermal behavior of PET, PTT, and their blends with various compositions was conducted with a differential scanning calorimeter (DSC) (Perkin-Elmer Pyris 1 DSC) equipped with a liquid nitrogen cooling system. Both temperature and heat flow were calibrated by a standard sample of indium. The heat of fusion of indium (28.5 J/g)was used to calibrate the thermal response of the calorimeter. All samples were dried in a vacuum at 50°C for 12 h before the measurements. To avoid uneven thermal conduction of the samples, which may cause different amounts of broadening and shifting of the peak positions, the aluminum pans were always filled with the same quantity of specimen, about 5 mg. The samples were sealed in the aluminum pans and heated above 280°C for 5 min to eliminate previous thermal histories. For the determination of glass transition temperatures, the samples were cooled to 10°C at a rate of 300°C/min to attain the completely amorphous state.

The glass transition (T_g) , cold crystallization (T_{cc}) , and melting temperatures (T_m) were determined from the second heating scan at a rate of 20°C/min over the range 0–280°C. The T_g was taken from the second heating scan as the midpoint of the heat capacity change with temperature. To observe the equilibrium melting point (T_m^0) of PET, PTT, and PET/PTT blends, the samples were first melted at 280°C for 5 min under a nitrogen atmosphere to eliminate the crystalline residues. Then, they were subsequently quenched at a rate of 300°C/min to the desired crystallization temperature (T_c) . After isothermal crystallization for 10 h at T_{cr} the samples were immediately heated up form T_c to 280°C at a rate of 20°C/min. The peak temperature of the endotherm was considered as the melting point of the sample.

The morphology of the blends was examined using a scanning electron microscope (SEM) (PHLIPS XL-30 ESEM-TMP). The samples for SEM were prepared to have enough thickness to ensure that the fractured surfaces can be conveniently examined. First, the blends were quenched by liquid nitrogen from melting state to amorphous state. Then the fractured surfaces of the blends were sputter-coated with gold (BAL-TEC SCD 005 Sputter Coater) for 60 s to give a 23 nm gold coating for SEM characterization.



45 0.2 0.4 0.6 0.0 Weight fraction of PTT Figure 2 T_g versus composition as Fox and Gordon-Taylor equation

Fox's Equation

75

70

65

60

55

50



Gordon-Taylor's Equation

0.8

1.0

Figure 1 DSC thermograms for the PET/PTT blends of various compositions. T_g is indicated by an arrow.

RESULTS AND DISCUSSION

Miscibility

The miscibility level and the crystalline characteristics of the blends were studied by DSC. Figure 1 shows the DSC thermograms for the melt-quenched PET/PTT blends samples with $T_{g'}$, $T_{cc'}$ and T_m temperatures against composition. T_g is indicated by an arrow.

The T_g can provide useful information on blend miscibility. One of the most commonly used criteria for establishing the phase behavior in amorphous binary polymer blends is the presence of one or more T_{g} s. If the blend is one-phase, a single T_{g} lying between the values for each component is detected and characterizes the mixture. If the blend is twophase, then two T_{g} s are observed close to or matching those of the two components. Thus, for an immiscible blend, two T_{g} s generally appear on the DSC scan, whereas for miscible blends or copolymers, only one T_g is observed.⁷ In Figure 1, all the blends showed a single T_g that depended on the composition. The T_g values of pure PET and PTT are 74 and 46°C, respectively. Moreover, the T_g values of the blends shift to lower temperatures with the increase of PTT content. This fact indicates the miscibility of the PET/PTT blends in the amorphous state. The dependence of T_g on blend composition can be evaluated by the classic Fox eq. (1) or Gordon-Taylor eq. (2) as follows:^{16,17}

$$\frac{1}{T_{g,\text{blend}}} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}} \tag{1}$$

where subscripts 1 and 2 represent PET and PTT, respectively; W_i is the weight fraction of component *i*; and *k* is the Gordon-Taylor parameter that equals $\Delta \alpha_1 / \Delta \alpha_2$, and $\Delta \alpha$ is the volume expansion coefficients difference between glassy and liquid states. Figure 2 shows the measured T_g as a function of PTT content in comparison with the fitting curves of the Fox equation and Gordon-Taylor equation.

It can be found that the measured T_g fit well with the predicted T_g value by the Fox equation and Gordon-Taylor equation with k = 1.295.

The miscibility of the PET/PTT blends in the amorphous phase could be evidenced by another thermal behavior, cold crystallization. In Figure 1, a single and composition dependent T_{cc} value can be observed for each sample. The composition dependence of T_{cc} of the blends is summarized in Figure 3.



Figure 3 Cold crystallization peak (T_{cc}) in PET/PTT blends.

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Figure 4 SEM graphs of the fractured surfaces of the quenched PET/PTT blends (5000 ×): (a) 90/10, (b) 80/20, (c) 70/30, (d) 60/40, (e) 50/50, (f) 40/60, (g) 30/70, (h) 20/80, (i) 10/90.

The T_{cc} of blends decreases nearly linearly with the low T_g component, PTT. The composition dependent behavior of T_{cc} in the blend can also be taken as a valid supportive evidence for miscibility.¹⁸

The single composition-dependent T_g and composition-dependent T_{cc} indicated that in PET/PTT blends, the polymer chains of PET and PTT are intimately mixed on fine molecular and segmental scales. These two intimately mixed chains act as a single chain segment with a single T_g in responding to external thermal changes. They also respond simultaneously to temperature changes in concerted ways and reorganize simultaneously which resulted in a single T_{cc} . All these features suggest that the miscibility of the PET/PTT blends in the amorphous state.

Morphology characterization

For morphology characterization, the PET/PTT blends of all composition in the melting state were rapidly quenched by liquid nitrogen in order to obtain the amorphous states. The fractured surfaces of the blends were observed by SEM at $5000 \times$ (Fig. 4).

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The SEM graphs showed complete homogeneity and lack of any discernible domains in the fractured surfaces of the quenched PET/PTT blends. The morphology evidence further supported the thermal analysis results of single composition-dependent T_g and composition-dependent T_{cc} . All evidence discussed above indicated a total miscibility of PET/ PTT blend in amorphous state at all compositions.

Melting behavior

From the subsequent melting thermograms after cold crystallization in Figure 1, only one melting point was found for PET/PTT blends with compositions of 90/10, 80/20, 70/30, and 10/90. However, two melting points around 256 and 226°C were found for the blends with compositions of 20/80, 30/70, 40/60, 50/50, and 60/40. The higher one is the melting point of PET crystal and the lower one is the melting point of PTT crystal. Because the DSC themograms showed two distinct melting peaks for some blends, it could be concluded that PET and PTT crystals coexisted in the blends. They did not form the cocrystals due to their different chemical



Figure 5 $T_{m,PET}$ and $T_{m,PTT}$ versus blend composition dependence.

structures. Figure 5 shows the observed T_m values for PET, PTT, and their blends versus blend composition dependence.

It can be found that the T_m of each component in the blends decreases with increasing content of the other component. The similar melting point depression phenomena have also been reported in other binary crystalline polymer blends, such as PET/PBT, PBT/PAr(I-100) and PBSU/PEO, etc.^{4,19,20} For miscible blends, the melting point of the crystalline component is usually lowered with respect to the pure polymer, as a result of thermodynamically favorable interactions.²¹ Thus, the melting point depression is used extensively to evaluate the miscibility of polymer blends. There are two basic origins of melting point depression: morphological and thermodynamic.²² Morphological variables such as lamellar thickness and crystal perfection can profoundly affect the melting point.

To confirm the miscibility of the two polymers in the melt-state, the polymer–polymer interaction parameter is determined from T_m^0 depression method.²³ The T_m^0 was determined by Hoffman-Weeks extrapolation method using the eq. (3):^{24,25}

$$T_m = \frac{1}{\gamma} T_c + \left(1 - \frac{1}{\gamma} \right) T_m^0 \tag{3}$$

where T_m and T_m^0 are the experimental melting point and equilibrium melting point for the crystals produced at T_c in the blend, respectively. γ is the thickening ratio between the initial thickness of a chainfolded lamella and the final lamellar thickness.

Figure 6 describes the procedure of determining T_m^0 of PET and its PET/PTT blends according to the Hoffman-Weeks equation. In this procedure, the measured T_m of samples crystallized at T_c were plot-



Figure 6 Hoffman-Weeks plots for PET/PTT blends.

ted against T_c . Data of 60/40, 50/50, 40/60, 30/70, and 20/80 blends were dropped off due to coexistence of PET and PTT crystals that was analyzed by DSC (Fig. 1). Thus, the samples used in Figure 6 contained the PET crystals only. Each piece of experimental data was obtained by isothermal crystallization for 10 h. It can be observed an increase in T_m with the T_c . By extrapolation of $T_m \sim T_c$ plot to T_m = T_c line, the value of T_m^0 can be obtained from the intersection at the $T_m = T_c$ line and the γ value can be obtained from the slope of $T_m \sim T_c$ line. The values of T_m^0 and γ are listed in Table I.

It can be found in Table I that the thickening ratio γ decreased with the increase of PTT content. This indicated that the PET crystals became less stable due to the smaller lamellar thickness that resulted in the melting point decrease.

The equilibrium melting point data in PET/PTT blends can be analyzed by the Nishi-Wang equation based on the Flory-Huggins theory:^{23,26}

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}} \left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) \phi_1 + \chi_{12} \phi_1^2 \right] \quad (4)$$

where the subscripts 1 and 2 denote the amorphous and crystalline components, respectively; T_m^0 and T_m are the equilibrium melting points of the pure crystalline component and its blends; V_u is the molar volume of the polymer repeating unit; *m* is the

 TABLE I

 Hoffman-Weeks Analysis for PET in PET/PTT Blends

T_m^0 (°C)	γ
279.6	2.303
278.3	2.240
276.9	2.219
275.3	2.107
	$\begin{array}{c} T_m^0 \ (^\circ C) \\ 279.6 \\ 278.3 \\ 276.9 \\ 275.3 \end{array}$

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Figure 7 $(1/T_m - 1/T_m^0)/\phi_1$ versus ϕ_1/T_m form the melting point depression of PET.

degree of polymerization; *R* is the universal gas constant; ΔH_u is the perfect crystal heat of the crystalline component; ϕ is the volume fraction of the component in the blend; and χ_{12} is the polymer–polymer interaction parameter. Because the degree of polymerization *m* is very large for polymers and the entropy of mixing could be negligible, then the equation can be simplified as Nishi-Wang equation:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}}\chi_{12}\phi_1^2 \tag{5}$$

It is well known that the melting point of a polymer is affected not only by thermodynamic factors but also by morphological parameters such as the crystal thickness, the equilibrium melting point of the polymer is used here in order to separate morphological from thermodynamic effects in analysis of meltingpoint depression. Equation (5) showed that a melting point depression would yield a negative χ_{12} value for the blend, which indicated a miscibility of the blends. According to the Nishi and Wang formulation, the interaction energy density *B* characteristic of the polymer pair can be defined as:²³

$$B = \chi_{12} R T / V_{1u} \tag{6}$$

Substitution eq. (6) into eq. (5) yields a linear relationship between $(1/T_m - 1/T_m^0)/\phi_1$ and ϕ_1/T_m :

$$\frac{1}{\phi_1} \left[\frac{1}{T_m} - \frac{1}{T_m^0} \right] = -\frac{BV_{2u}\phi_1}{\Delta H_{2u}T_m} \tag{7}$$

Equation (7) was used to plot the melting-point depression and to give the interaction energy density value. According to DSC analysis in Figure 1, in construction of the plots using eq. (7), we assume that for blends with PTT contents of less than 30%, PET

is considered to be the crystalline component, whereas PTT is considered to be the amorphous component rejected from the crystalline phase. The following values were used with eq. (7): for PET, $\Delta H_{\rm PETu} = 25.9 \text{ kJ/mol},^{26} V_{\rm PETu} = 139.8 \text{ cm}^3/\text{mol}^{26}$; for PTT, $V_{\rm PTTu} = 149.6 \text{ cm}^3/\text{mol}.^{18}$ Figure 7 shows the plot of eq. (7) for the PET/PTT blends, assuming the melting point of PET was depressed by the addition of PTT component. A straight line fitted with the least-square method was obtained.

From the slope value of the fitting straight line in Figure 7, the interaction energy density B = -4.932 J/cm³ and the polymer–polymer interaction parameter $\chi_{12} = -0.1634$ can be obtained. The negative values of *B* and χ_{12} for the PET/PTT system indicate that the polymer pair can form a thermodynamically stable miscible mixture at temperatures above the melting point. In addition the magnitude of the χ_{12} value appears to be quite reasonable in comparison with data obtained for other miscible polymer blends.^{21,23}

Melting crystallization behavior

Figure 8 shows the melting crystallization DSC thermograms for PET, PTT, and their blends during cooling at a rate of 20°C/min.

From Figure 8, it can be observed a single and composition dependent melting crystallization temperature (T_{mc}) for each sample. The results showed that in the PET/PTT blends, PET and PTT crystallized simultaneously which indicated that an attractive interaction exists between PTT and PET components.



Figure 8 Melting crystallization DSC thermograms for the PET/PTT blends of various compositions.

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Figure 9 Melting crystallization temperature $T_{\rm mc}$ versus blend composition dependence.

Figure 9 shows the observed $T_{\rm mc}$ values for PET, PTT, and their blends versus blend composition dependence. From Figure 9 we can see that the melting crystallization temperature $T_{\rm mc}$ is gradually reducing and then increasing with the increase of the PTT component.

Crystallization is a process of arrangement of molecules from disorder to order. As analyzed above, PET/PTT system is a thermodynamically stable miscible mixture at temperatures above the melting point. Thus, the two kinds of polymer chains are liable to interpenetrate and entangle one another in the melting state and crystallize simultaneously which presented a single T_{mc} for each sample in Figure 8. However, the DSC themograms (Fig. 1) showed two distinct melting peaks for some blends, it could be concluded that PET and PTT chains formed their own crystals respectively and they did not form the cocrystals due to their different chemical structures. In the melting crystallization process of the PET/PTT blends, the interpenetrating and entangling of the two kinds polymer chains reduced the segmental mobility and hindered the ordered arrangement of the PET and PTT polymer chains to form their own crystals, respectively. This hindrance effect increases with the increase of the ratio of the two kinds polymer chains. That is to say, the closer are the amounts of the two kinds polymer chains, the more obvious is the hindrance effect. Because of this reason, in Figure 9, the melting crystallization temperature T_{mc} decreased with an increase of the minor component in the blends and the 50/50 sample showed the lowest $T_{\rm mc}$ value.

CONCLUSION

The miscibility and crystallization behavior in PET/ PTT blends have been investigated. These blends exhibit a single composition-dependent glass transition and cold crystallization peak over entire composition range. The SEM graphs also showed complete homogeneity in the fractured surfaces of the quenched PET/PTT blends. All these indicated that a total miscibility of PET/PTT blend in amorphous state at all compositions. The polymer–polymer interaction parameter χ_{12} and interaction energy density *B* were calculated from the equilibrium melting depression of PET using the Nishi-Wang equation. The negative values of χ_{12} and *B* indicate that PET/PTT blends are thermodynamically miscible in the melting state. The melting crystallization behavior of the blends is also related to its miscible nature in the melting state.

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