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Phase Morphology and Thermal Characteristics of Binary Blends Based on PTT and PA12

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Summary

Phase morphology, miscibility and thermal properties of a binary blend, poly-(trimethylene terephthalate) (PTT) / polyamide-12 (PA12), were examined and found to be immiscible showing a phase-separated morphology. DSC cooling data of the blends indicates that the melt crystallinity of PTT phase increases, with respect to pure state, upon blending with PA12 while that of polyamide phase declines in the presence of PTT phase implying that polyester molecules reduces the crystallization ability of polyamide phase. Also, PA12 in that blend where it is minor phase shows a fractionated crystallization. A significant cold crystallization exotherm supposed to be due to the reorganization of polymeric chains was exhibited by PTT phase in DSC second heating thermograms which its degree was raised upon blending with PA12. DMA graphs reveal a single tan δ peak due to the fact that the glass transition of the respective constituents overlap and a single peak comes into view. Therefore, DMA can not be solely used to assess the miscibility in this system.

Introduction

Blending has emerged as a conventional strategy to develop new materials with tailor-made characteristics. The ultimate performance of the resultant blend is considerably controlled by phase morphology and crystallinity of the system. Blend morphology is affected by rheological characteristics of the base polymers, and shear stress applied during the mixing of the components [1,2]. The last significant factor in controlling the ultimate performance of the blend is the total crystallinity which usually shows a complex behavior especially where the component polymers are semicrystalline and intrinsically immiscible [3,4]. A systematic study on these two significant factors helps one to achieve a blend with optimized properties.

Poly (trimethylene terephthalate)(PTT), an aromatic polyester recently introduced by Shell Chemicals, has drawn great attention because of possessing a significant combination of prominent properties of poly(ethylene terephthalate) (PET) and processing characteristics of poly (butylene terephthalate) (PBT) [5]. Due to various reasons, blending of aromatic polyesters, PBT and PET, with aliphatic polyamides has been of significant concern frequently studied by numerous researchers [3,4,6-18].

This contribution intends to describe the morphology, melting, crystallization, and dynamic mechanical behaviors of binary blends composed of PTT and polyamide-12 (PA12).

Experimental

Materials

All the materials of this study were commercial grades used as received without any further treatment. PTT available as CORTERRA®, grade 200, was obtained from Shell Chemicals Co. PA12 available as Grilamid®, grade L25, was provided with EMS-CHEMIE (Germany). To minimize the moisture content, both PTT and PA12 were dried for 24 h at 80°C *in vacuo* prior to melt blending.

Instruments

PTT/PA12 blends were prepared in a conical twin-screw extruder, DACA Micro-Compounder (DACA Instruments). Mixing time of 10 min, screw speed of 100 rpm, and temperature of 230°C were fixed for samples preparation. The micro-compounder showed a high torque on initial feeding which progressively dropped indicative of melt blends uniformity.

Morphology of the cryogenically fractured surface of the extruded strands subsequently to the coating with a thin layer of gold, was examined by a Cambridge S-360 Scanning Electron Microscope (Cambridge Instruments).

Dynamic mechanical properties in the solid state were examined by a 2980 DMA (TA Instruments) to determine the viscoelastic properties in bending mode. Rectangular specimens of dimension 10 mm × 10 mm × 0.5 mm were employed for testing. Samples were heated from 0°C to 150°C at a heating rate of 3 K/min and frequency of 1 Hz. Also, DMA meausuremnts of neat components in the melt state were carried out using ARES oscillatory rheometer (Rheometric Scientific) with a parallel plate geometry (diameter 25 mm and gap of 1.5 mm) at 230 °C under inert ambient.

Differential scanning calorimetry measurements were performed on a 2920 MDSC (TA Instruments) with samples of about 10 mg sealed in aluminum pans under nitrogen atmosphere. The samples were first heated at a rate of 10 K/min from 20°C to 250°C and kept there for 5 min in order to erase all thermal history, subsequently cooled down to 20°C at the same rate and the dynamic crystallization behavior were recorded. Also, the second heating scan within the same range at 10 K/min was applied to assess the melting characteristics of the controlled crystallized blends.

Calculation of crystallization degree

Degree of melt crystallinity for each component in the blends was calculated in terms of the following expression:

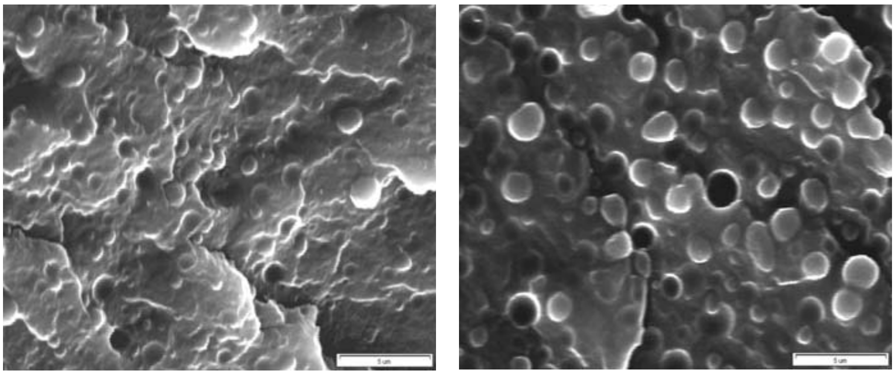
$$X_c = (\Delta H_c / w_c \, \Delta H^{\circ}_m) \times 100 \qquad \textbf{(1)}$$

in which ΔH_c denotes the melt crystallization enthalpy of the component in the sample, w_c refers to the weight fraction of the component in the blend, and ΔH°_m is the enthalpy of fusion of 100 % crystalline component based on the literature data (for pure PTT, ΔH°_m=140 J/g [5] and for pure PA12, ΔH°_m=233.5 J/g [19]). Similar equation in which ΔH_c was replaced with cold crystallization enthalpy was applied to estimate the degree of cold crystallinity.

Results and Discussion

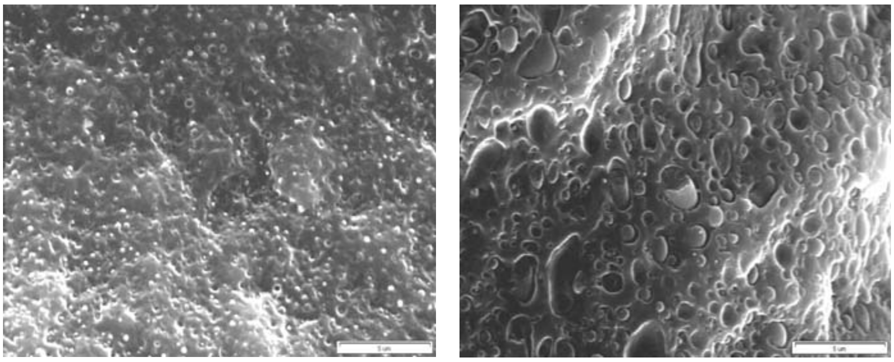
Phase Morphology

SEM examinations (Figures 1 and 2) reveal a two-phase morphology showing immiscibility of PTT/PA12 system as expected from previous reports on similar blends [3,4,8-12]. Figure 1a,b displays SEM micrographs of PTT/PA12 90/10 and 75/25 blends where the dispersed phase is polyamide. It is observed that in higher dispersed contents, the particle size increases due to coalescence phenomenon. The same trend is indicated in Figure 2a,b wherein polyester forms the dispersed phase (PTT/PA12 10/90 and 25/75). It is inferred from comparing the micrographs of



(a) (b)

Figure 1. SEM micrographs of (a) PTT/PA12 90/10 and (b) PTT/PA12 75/25



(a) (b)

Figure 2. SEM micrographs of (a) PTT/PA12 10/90 and (b) PTT/PA12 25/75

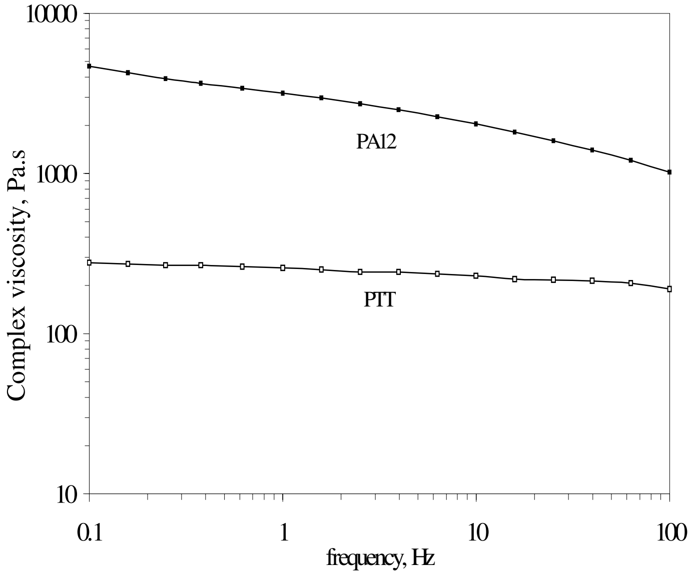


Figure 3. Complex viscosities of neat components at 230 °C plotted versus angular frequency

Figures 1 and 2, that the particle size in those blends with PA12 as the dispersed phase is higher. The reason essentially refers to the blend viscosity ratio. Since the magnitude of complex viscosity of PA12 is notably higher than that of PTT over the whole range of frequency (Figure 3, assuming Cox-Merz rule [20] holds), then in the system with PA12 as dispersed phase, the viscosity ratio becomes remarkably high which is unfavorable to fine dispersion and accordingly the interfacial forces dominate making the droplet breakup difficult leading to larger phase domains ultimately [1,2]. Also, based on Figure 4, PTT/PA12 system shows a droplet morphology rather than co-continuity at mid-composition range. This is not in contrast with the predictions of relevant theories [2] which correlate the rheological data and morphological observations.

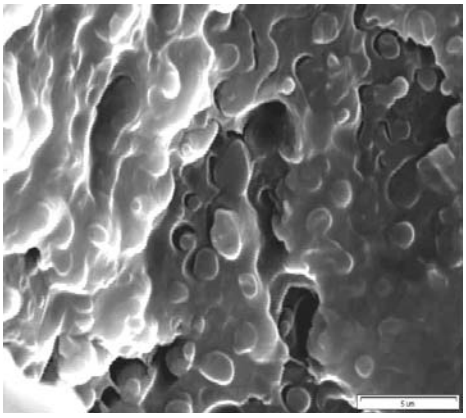


Figure 4. SEM micrograph of PTT/PA12 blend at mid-range composition (50/50)

Thermal Analysis

Melt Crystallization Behavior. Figure 5 displays the DSC thermograms at the cooling scan for PTT/PA12 binary blends along with those of the constituents recorded after erasing all thermal history. According to this figure, each neat component shows a well-defined exotherm associated with its melt crystallization process (PTT at 179°C and PA12 at 149°C). One pronounced exotherm corresponding to PTT-rich phase and a less significant peak associated with PA12-rich phase appear on PTT/PA12 75/25 thermogram. In addition, a minor peak at 129°C arises that can be assigned to the fractionated crystallization of polyamide phase. This phenomenon has frequently been reported in various blends [21,24]. In DSC thermogram of PTT/PA12 25/75, it is noticed that the main exotherm of PTT disappears and only a single significant peak corresponding to PA12-rich phase is detectable. However, a new broad exotherm appears in this thermogram at 123°C which can be assigned to the retarded melt crystallization processs of PTT phase contributed by the presence of PA12 crystallites as active nuclei. The lack of active nuclei at low supercooling causes a delay in melt crystallization phenomenon of PTT phase. Table 1 presents the melt crystallization temperatures ($T_{c,m}$), melt crystallization enthalpies (ΔH_c) and melt crystallinity (X_c) of each phase derived from Figure 5. It is clearly observed that upon decreasing the amount of a component in a sample, the value of ΔH_c diminishes. The values of crystallization enthalpy have been used to calculate degree of crystallinity as already described in experimental section. Interestingly, the crystallinity of PTT-rich phase in the blends increases while that of PA12 decreases showing that the presence of PTT phase reduces the overall melt crystallization ability of PA12 molecules, while the presence of polyamide is favorable to melt crystallinity of PTT. Similar results on various immiscible systems are also available in the literature [25].

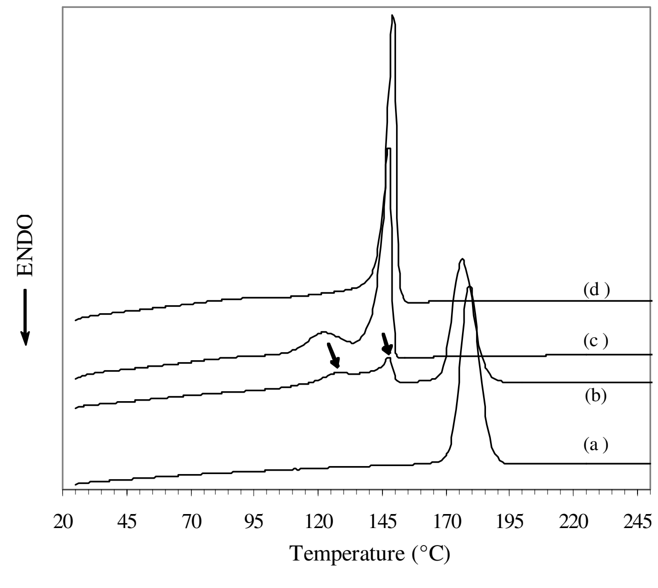


Figure 5. DSC thermograms of the constituents and blends at cooling cycle: (a) neat PTT ; (b) PTT/PA12 75/25 ; (c) PTT/PA12 25/75 ; (d) neat PA12

Table1. Summary of PTT/PA12 DSC results

Sample	$T_{c,m}$ (°C)		$T_{c,c}$ (°C)		T_m (°C)		ΔH_c (j/g)	
	PTT	PA12	PTT	PA12	PTT	PA12	PTT	PA12
PTT	179	-	207	-	228	-	9.10	-
75/25	176	147	206	-	228	176	7.02	1.73
25/75	-	148	190	-	226	177	2.60	7.24
PA12	-	149	-	-	-	178	-	10.78

Table1. (continued)

Sample	ΔH_m (j/g)		X_c(%)	
	PTT	PA12	PTT	PA12
PTT	-10.26	-	39.0	-
75/25	-7.54	-1.60	40.1	17.8
25/75	-1.90	-6.56	44.5	24.7
PA12	-	-9.20	-	27.7

Subsequent Melting Behavior. DSC thermograms at the second heating scan for the constituents and their blends are given in Figure 6. Glass transition temperatures can not be detected from these thermograms. Both melting endotherms respective to the constituents have a shoulder on the right side showing a sequential melting behavior of the neat components which is in line with the literature observations and its origin refers to the presence of different crystalline structures with different stabilities [26]. Furthermore, a well-defined exotherm associated with PTT cold crystallization is identified at 207°C which is due to the reorganization (recrystallization) phenomenon of PTT chains [27].

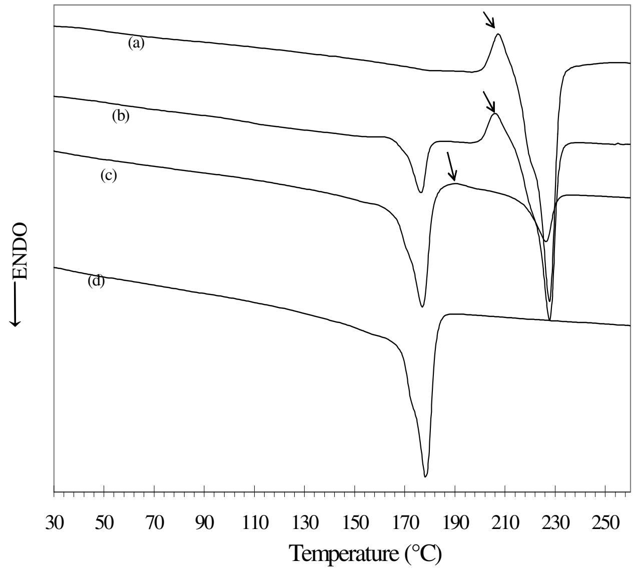


Figure 6. DSC thermograms of the constituents and blends at the second heating cycle :
(a) neat PTT ; (b) PTT/PA12 75/25 ; (c) PTT/PA12 25/75 ; (d) neat PA12

DSC thermagrams of the blends, according to Figure 6, show two substantial endotherms (melting temperature,T_m) respective to each phase which reveal no significant shift upon blending, as indicated in Table 1. Also, the value of fusion enthalpy (ΔH_m) of each component decreases with decreasing its amount in the blend. Interestingly, PTT cold crystallization exotherm peak ($T_{c,c}$), as demonstrated in Table 1, shifts from 206°C in PTT/PA12 75/25 to 190°C in 25/75 implying that the presence of PA12 molecules affects the reorientation process of PTT chains. Also, the cold crystallinity of PTT phase increases from 5 % in pure state to ca. 6% in PTT/PA12 75/25 and ca. 13% in PTT/PA12 25/75 meaning that PA12 molecules contributes to the cold crystallization phenomenon of PTT.

Dynamic Mechanical Analysis. Since DSC curves are not sensitive enough to detect the glass transitions, DMA is mostly used to obtain the values of glass transition temperatures as well as to assess the blend miscibility. Figure 7 shows the tan δ variation of the blends along with that of the constituents. Two maxima appear in tan δ curve of PA12. The low-temperature peak corresponds to the glass transition temperature (T_g) and the high-temperature one (at 135°C) is probably assigned to the crystalline phase transitions, however PTT reveals only a single peak associated with glass transition. Tan δ curves for the blends show a single broad peak, however it can not be translated into the miscibility, since the difference between T_g values of PTT and PA12, as derived from loss modulus curves (Figure 8) and indicated in Table 2, is insufficient to be appeared on DMA graphs separately. Therefore DMA can not be solely used to assess the blend miscibility in this system. Figure 8 also shows the diagrams of the tensile storage modulus, which is a criterion for stiffness, versus temperature. It is clearly observed that the stiffness of samples increases as the amount of PTT rises. However it should be mentioned that the values of tensile storage

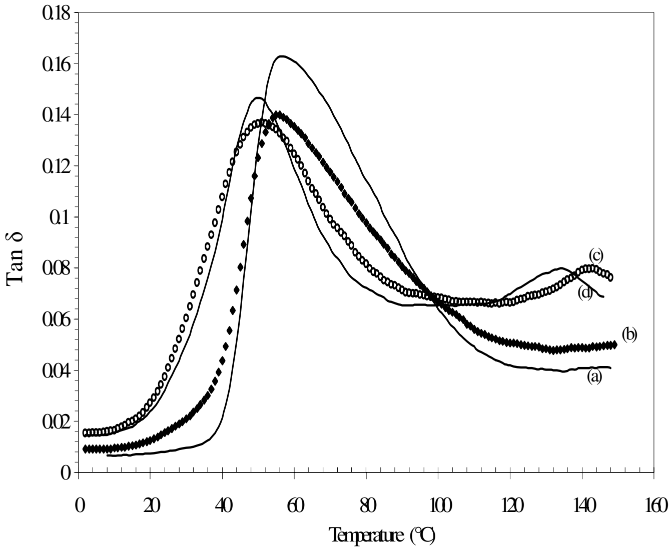


Figure 7. Tan δ curves of the constituents and blends : (a) neat PTT ; (b) PTT/PA12 75/25 ; (c) PTT/PA12 25/75 ; (d) neat PA12

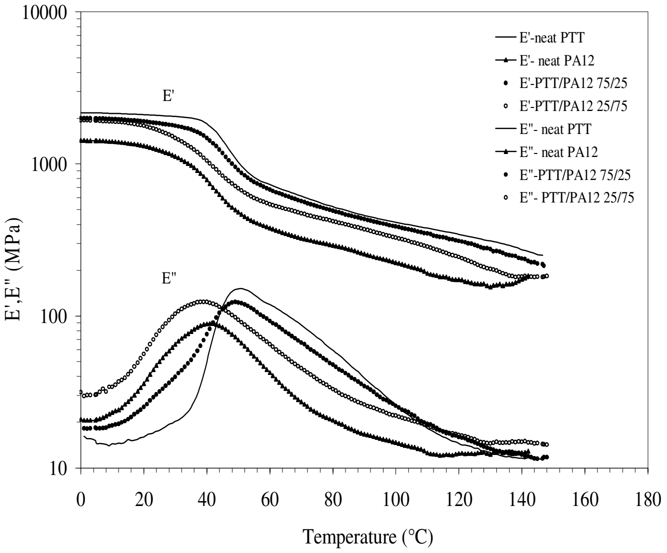


Figure 8. Tensile storage and loss moduli of the constituents and blends against temperature

modulus (stifness) of the blends (75/25 and 25/75) before glass transition region are almost the same which may be ascribed to the equality of the crystallinity present in the samples before increasing the temperature and reaching the transition region. This can be verified by the data (X_c) given in Table 1.

Table 2. Glass transition temperatures of PTT/PA12 estimated using loss modulus curves

Sample	PTT	PTT/PA12 75/25	PTT/PA12 25/75	PA12
T_g (°C)	50	48	39	41

Conclusions

Blends of PTT and PA12, as observed by SEM, were found to be immiscible having a phase-separated morphology. DSC cooling data of the blends indicated that the melt crystallinity of PTT phase increases upon blending with PA12 with regards to neat state, while that of polyamide phase declines in the presence of PTT phase suggesting that polyester molecules reduces the crystallization ability of polyamide phase. Also, PA12 in that blend where forms dispersed phase, shows a fractionated crystallization. A significant cold crystallization exotherm supposed to be due to the reorganization of polymeric chains was exhibited by PTT phase in second heating thermograms which its degree was raised upon blending with PA12. DMA graphs reveal a single tan δ peak because the glass transition of the respective base polymers overlap and a single peak comes into view. Therefore, DMA can not be solely used to assess the miscibility in this system.

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