

Miscibility, Melting, and Crystallization of Poly(trimethylene terephthalate)/Poly(ether imide) Blends

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ABSTRACT: Miscibility, melting, and crystallization behaviors of solution-blended poly(trimethylene terephthalate) (PTT)/poly(ether imide) (PEI) blends have been investigated using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and polarized light microscopy (PLM). These blends show a single and composition-dependent glass transition temperatures over the entire composition range, implying that these blends are fully miscible in the amorphous region. The enthalpy of the middle endotherm melting of the primary crystallization decreases with increasing PEI content in the blend. Recrystallization of PTT during heating scan in DSC is either retarded or fully inhibited by the presence of PEI. In nonisothermal crystallization, the depression of crystallization temperature of PTT also depends on the blend composition and cooling rate; the presence of PEI decreases the PTT segments migrating to the crystallite-melt interface. The effects of temperature and PEI content on the spherulite growth rate of PTT were evaluated by PLM. The spherulite growth rate decreases with the increase of the PEI content, implying that it is a thermodynamically dominant process. Both thermodynamic and kinetic factors cause total inhibition of PTT crystallization at higher PEI content in the blend. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 850–856, 2002; DOI 10.1002/app.10367

Key words: miscibility; melt; crystallization; poly(trimethylene terephthalate) (PTT); poly(ether imide) (PEI)

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is a linear aromatic polyester with three methylene moieties in the repeating unit. Although chemical structures are similar, the physical properties of PTT are much different from that of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). PTT possesses good mechanical properties that has been developed by Shell Chemical Company for an engineering thermoplastic and as a matrix for fiber-reinforced composites.^{1,2} However, lower glass transition temperature ($T_g = 44^\circ\text{C}$) of PTT is a disadvantage

in some applications. On the contrary, poly(ether imide) (PEI) is a high-performance engineering plastic with a T_g of about 215°C . Besides, PEI possesses several advantageous properties such as excellent toughness and good electrical insulation. But due to its amorphous nature, PEI is poor for chemical resistance. Therefore, it is expected that blending of PTT and PEI will offer an interesting route to combine the complementary properties of both polymers. Blending of a semicrystalline and an amorphous polymer, the melting and crystallization behaviors of the crystalline polymer are expected to be changed. Similar studies on PET/PEI,^{3–5} and PBT/PEI^{6,7} blends have been reported previously. It was reported that PET/PEI blends are miscible over the whole composition range in the melt.⁴ Because of the similar chemical structures be-

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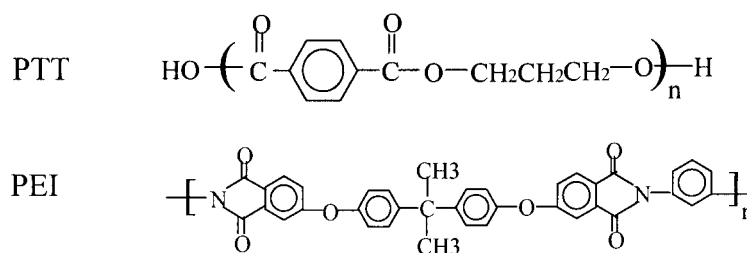
tween PET and PTT, it is interested to explore the miscibility and crystallization behavior of PTT/PEI blends. According to our knowledge, no prior study has been reported on PTT/PEI blends. In our previous studies,^{8,9} we have reported the multiple melting behavior and crystallization kinetics of the PTT.

EXPERIMENTAL

Materials

Poly(trimethylene terephthalate) (PTT) was obtained from the Shinkong Synthetic Fibers Co.

(Taiwan) in the form of pellets. The intrinsic viscosity (I.V.) of the PTT in a 60 : 40 mixed solvent of phenol and tetrachloroethane at 25°C was measured to be 0.80 dL/g. The weight and number-average molecular weights determined by gel permeation chromatography (GPC) were 46,300 g mol⁻¹ and 21,050 g mol⁻¹, respectively. The molecular weight distribution was 2.2. PEI used in this study was obtained from General Electrical (GE, Ultem 1000), and its molecular weights are 12,000 and 30,000. The chemical structures of PTT and PEI are shown as follows:



Blends Preparation

All the blends of PTT and PEI were carried out by solution precipitation. A series of PTT/PEI blends of designated composition ratios were stirred and dissolved in dichloroacetic acid at 80°C. These blends were subsequently recovered by precipitation in 10-fold excess volume of water. The blends were thoroughly washed with a large amount of water and then dried in a vacuum oven at 105°C for 3 days.

Thermal Analysis

The measurements of weight loss of the PTT/PEI blends were performed on a Perkin-Elmer thermogravimetric analysis system TGA-7 from 30 to 700°C under a nitrogen atmosphere. The heating rate employed was 10°C/min. The thermal properties of PTT, PEI, and its blends were determined using a differential scanning calorimetry (Perkin-Elmer DSC-7) under a nitrogen atmosphere. For the glass transition temperature (T_g) measurement, about 4 mg of specimen was placed in a DSC pan and maintained at 260°C for 10 min. The sample was immediately quenched by liquid nitrogen. Upon reheating at 10°C/min from 10 to 260°C, an inflection point as the T_g was

observed. For isothermal crystallization study, the sample was first heated to 260°C and maintained at this temperature for 10 min, then cooled at a rate of 300°C/min to the predetermined temperature of 200°C. At this temperature crystallization for 60 min, followed by reheating the sample to 260°C at a rate of 10°C/min. For nonisothermal crystallization study, the sample was melted and then cooled from 260°C to room temperature at various rates (2, 5, 10, 20°C/min). The crystallization temperatures and crystallization heats for all specimens are obtained from the cooling curves.

Spherulite Growth Rate Measurement

Measurement of the radius growth rate of PTT crystallites under isothermal crystallization was investigated using a polarized light microscopy (Leitz LABORLUX 12POLIS) equipped with a heating stage (Linkam THMS-600), a temperature control system (Linkam TP-92), and a video recording system. Specimen was prepared by melting the PTT sample on a glass slide on a heating stage at 260°C, followed by pressing of the melted sample with a piece of cover glass and maintained for 5 min at this temperature to remove any thermal history. Then the sample was

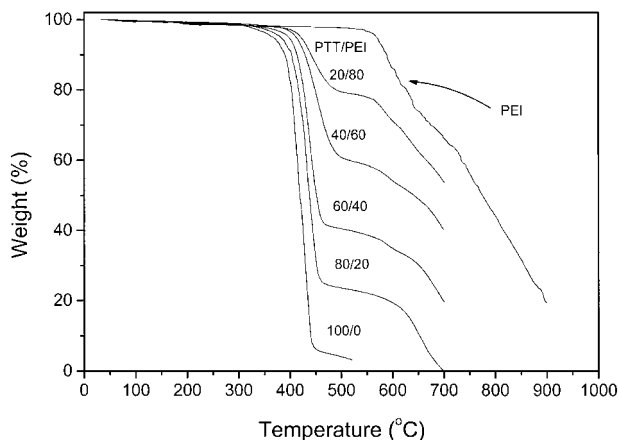


Figure 1 TGA thermograms for PTT, PEI, and PTT/PEI blends.

rapidly quenched to the predetermined crystallization temperature. The subsequent growth of a particularly selected PTT spherulite was viewed between crossed polars and recorded by a video camera at appropriate time intervals. The spherulitic radius was measured directly from the video-record image. By plotting crystal radius vs. time, the slope of the line or the spherulite growth rate at different temperatures (180–208°C) can be obtained.

RESULTS AND DISCUSSION

Thermal Stability

Thermal stability of a polymeric material is one of the most important properties for both processing and application. Thermogravimetry analysis is the most widely used method to characterize thermal stability of polymers. Figure 1 shows the thermal weight loss curves for PTT, PEI, and PTT/PEI blends. The PTT exhibits a well thermal stability below 300°C, begins to decompose at around 320°C. The 5% weight loss temperature is at about 367°C, and the PTT is completely decomposed at 450°C, leaving about 6% residue. From the result of TGA analyses, PTT can be considered as a thermally stable polymer. Therefore, no decomposition is expected in DSC and PLM experiments, because these operation temperatures are below 300°C. In Figure 1, it is evident that the weight loss of PTT/PEI blends exhibits two stages. The first stage decomposition corresponds to the PTT component, and the second stage is for the PEI component. It is noted that the ratio of

weight loss is identical to the blend composition. Furthermore, the 5% weight loss temperature of the specimen increases with increasing PEI content in the blend. Thus, from this result it is concluded that blending with PEI may improve the thermal stability of the PTT.

Miscibility of PTT/PEI Blends

Differential scanning calorimetry has been extensively used to investigate miscibility in polymer blends. Figure 2 shows DSC traces for quenched PTT, PEI, and PTT/PEI blends at a heating rate of 10°C/min. Essentially only one T_g is observed for all compositions, and the T_g s of the PTT and PEI are at 44 and 217°C, respectively. As can be seen, the T_g rises monotonically with the increase of the PEI content in the blend, indicating fully miscibility of these blends. Furthermore, both the cold crystallization temperature (T_{cc}) and its width of the exotherm increase with increasing PEI content, as shown in Figure 2. These results imply that the presence of PEI retards PTT crystallization from the glassy state, which is normally expected from a miscible polymer pair. No trace of melting endotherm can be observed for the blend containing PTT less than 50%. This result is similar to previous study on PET/PEI blends.³ Figure 3 plots the glass transition temperature as a function of PEI content for quenched PTT/PEI blends. For a miscible poly-

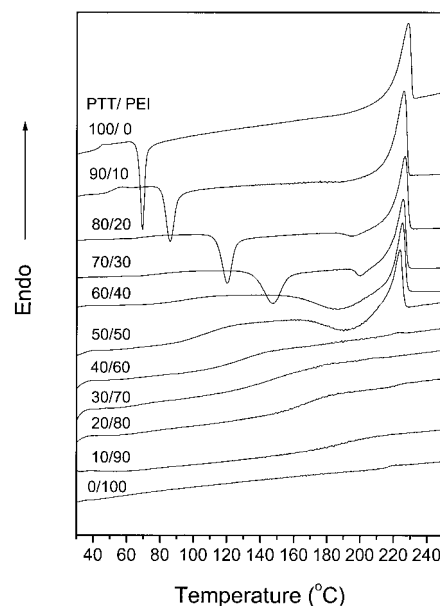


Figure 2 DSC scans for quenched PTT, PEI, and PTT/PEI blends at a heating rate of 10°C/min.

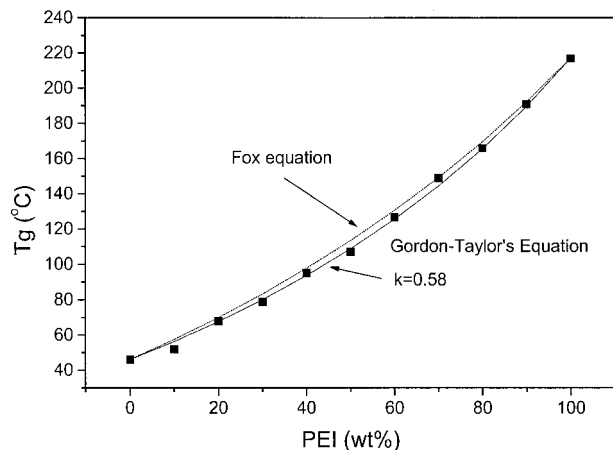


Figure 3 Glass transition temperature as a function of PEI content for quenched PTT/PEI blends.

mer blend system, a number of equations have been proposed to describe the composition dependence of T_g of the blend. One of the most frequently used expressions is the Fox equation.¹⁰

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where w_1 and w_2 are weight fraction of components 1 and 2. It appears that measured T_g does not fit well with the predicted T_g value (dashed line) by the Fox equation, as shown in Figure 3. On the contrary, the Golden Taylor's equation¹¹ provides a satisfactory description for the T_g -composition relationship.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2)$$

where k is the adjustable parameter, and $k = 0.58$ is suitable for this blend system.

Figure 4 shows the glass transition width against the PEI composition for the quenched PTT/PEI blends. As can be seen, in all case the glass transition width is wider for the blends than that for the pure PTT and PEI components. The maximum T_g width is found in the blend containing 70% PEI. A prior study on PET/PEI blends gave the similar result, in which the T_g width exhibits a maximum at the intermediate blend composition.³ Figure 5 plots melting temperatures (T_m) and cold-crystallization temperatures (T_{cc}) of the blend against the weight fraction of PEI where T_m and T_{cc} of PTT are at 228 and 70°C, respectively. By increasing PEI content in the

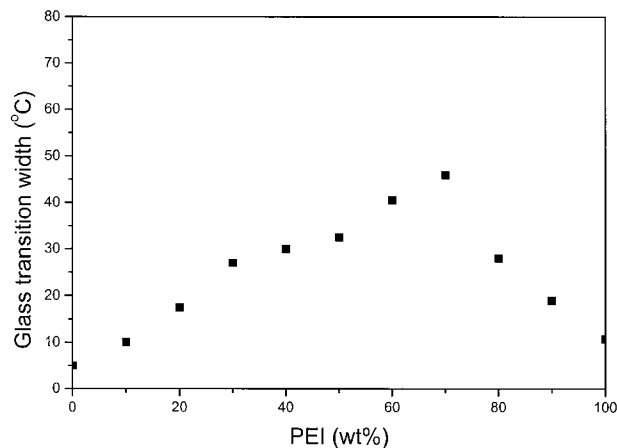


Figure 4 Glass transition width as a function of PEI content for quenched PTT/PEI blends.

blend, the melting temperature gradually decreases from 228 to 224°C. On the contrary, the cold crystallization temperature of the PTT increases with increasing PEI content, indicating that the crystallization rate of PTT decreases with increasing PEI content in the blend. The observation of T_g behavior, melting temperature depressing, and the cold crystallization temperature increasing suggest that the intermolecular interaction between PTT and PEI is responsible for these phenomena.

Melting Behavior

The melting endotherms of PTT/PEI blends after isothermal crystallization at 200°C for 60 min are shown in Figure 6. It can be seen that the pure PTT displays two melting endotherms at 220 and

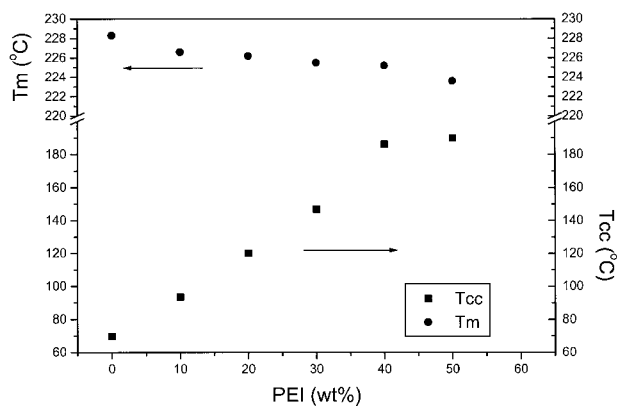


Figure 5 Melting temperatures and cold-crystallization temperatures of the PTT component in PTT/PEI blends.

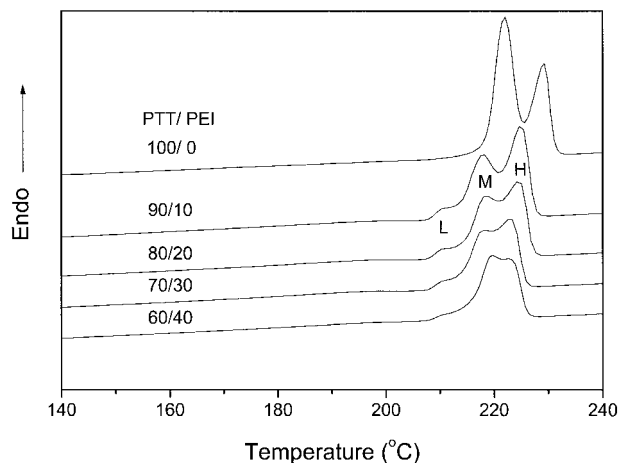


Figure 6 DSC heating curves for PTT/PEI blends isothermally crystallized at 200°C for 60 min.

228°C. Different crystal structures have been reported to cause the multiple melting endotherms for isotactic poly(propylene) and poly(vinylidene fluoride).^{12,13} Simultaneous melting, recrystallization, and remelting has been reported as the origin of the double melting of PET,¹⁴ Nylon 66,¹⁵ and isotactic polystyrene.¹⁶ Moreover, Lee et al.^{17,18} has reported that double melting endotherms of PEEK resulted from four contributions: partial melting of the original crystals, their recrystallization, melting of the recrystallized crystals, and melting of the core crystals. Similar to PEEK, PTT also shows double melting endotherms, which has been reported in our prior study.⁸ In Figure 6, there are three endotherms in PTT/PEI blends, which are denoted as L, M, and H, respectively, from lower to higher temperature. Peak L corresponds to the melting of crystals formed by a secondary crystallization process, peak M corresponds to the melting of the normalized primary crystallization, and peak H corresponds to the melting of crystals formed by a reorganization process during the DSC scan.¹⁹ The position of the L endotherm in Figure 6 located at about 210°C is only 10°C higher than the crystallization temperature. Moreover, the height of the H-endotherm relative to the M-endotherm decreases more rapidly with increasing PEI content in the blend. This is probably due to the fact that the recrystallization of PTT during DSC heating scan is retarded more severely upon blending with higher PEI content.

Crystallization Behavior

Figure 7 shows cooling thermograms of PTT crystallization in the pure form and various PTT/PEI

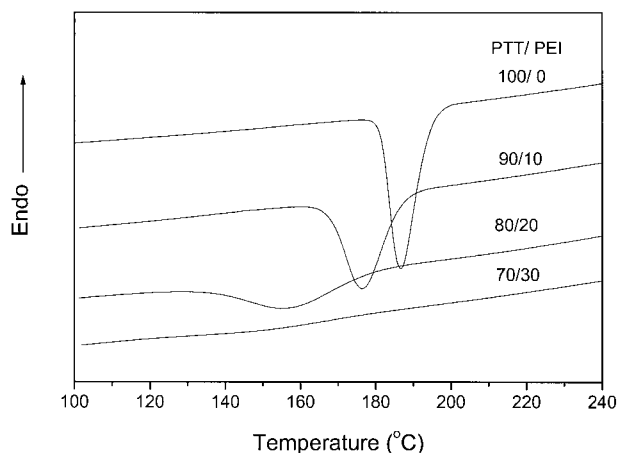


Figure 7 Thermograms of crystallization of PTT and its blends at the cooling rate of 10°C/min from melt.

blends at the cooling rate of 10°C/min from the melt, and the detailed data are summarized in Table I. There is an obvious depression in the crystallization temperature with the increase of PEI content and the crystallization exotherm of the PTT/PEI = 70/30 blend nearly disappears. When the PEI content is higher than 40% (not shown here), no crystallization exotherm can be detected, suggesting that the PTT component in

Table I Nonisothermal Crystallization Data of PTT/PEI Blends at Different Cooling Rates

Cooling Rate (°C)	Composition	Crystallization		
		Onset (°C)	Peak (°C)	ΔH_c^* (J/g)
2	PTT/PEI = 100/0	205.3	200.2	56.6
	PTT/PEI = 90/10	199.2	193.0	52.7
	PTT/PEI = 80/20	194.9	185.5	50.1
	PTT/PEI = 70/30	191.1	180.2	44.3
5	PTT/PEI = 100/0	198.4	191.2	51.4
	PTT/PEI = 90/10	193.3	184.9	48.2
	PTT/PEI = 80/20	187.1	171.8	44.1
10	PTT/PEI = 70/30	184.7	161.6	35.2
	PTT/PEI = 100/0	192.5	183.9	48.9
	PTT/PEI = 90/10	187.3	176.5	45.1
	PTT/PEI = 80/20	178.7	156.3	34.5
20	PTT/PEI = 70/30	174.8	152.1	4.6
	PTT/PEI = 100/0	185.0	175.3	46.6
	PTT/PEI = 90/10	179.3	165.9	38.2
	PTT/PEI = 80/20	169.3	142.8	15.7
	PTT/PEI = 70/30	—	—	—

^a The enthalpy of crystallization is based on PTT weight fraction in the blend.

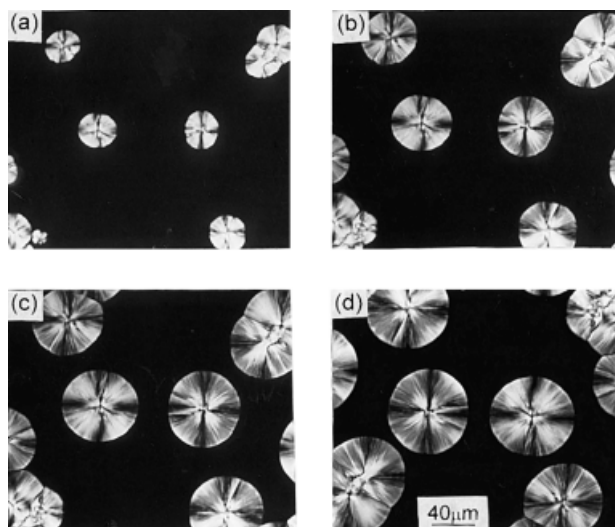


Figure 8 Polarized light micrographs of PTT isothermally crystallized at 204°C for various times: (a) 86 s, (b) 116 s, (c) 148 s, (d) 166 s.

these blends is unable to crystallize during the cooling scan. As shown in Table I, nonisothermal crystallization behaviors of these blends are found significantly affected by both cooling rate and composition. For a given composition, the crystallization temperature begins at higher temperatures when slower cooling rates are used. At a given cooling rate, the presence of PEI in the blend reduces the enthalpy of crystallization. It is clear that both the crystallization temperature and enthalpy of crystallization decrease with the increase in the cooling rate and PEI content. For a semicrystalline-amorphous miscible blend system, the depression of the crystallization temperature is influenced by several factors.^{20,21} First, the reduction of crystallizable polymer in the melt results in concomitant decrease in the thermodynamic driving force favoring crystallization. Second, the PTT component is diluted with PEI, the transport process of PTT segments to the crystallite-melt interface becomes more protracted and results in slower crystal growth rate. Third, from the thermodynamic consideration, the chemical potential of the crystallizable polymer in a miscible amorphous-crystalline blend is reduced because of the addition of the amorphous component and leads to a decrease in the equilibrium melting temperature of the blend. Finally, the T_g of the blend rises with the increase of the PEI content, which tends to increase melt viscosity and decreases diffusion rate of the PTT segments. For further investigation, the effect of crystallization

temperature on the crystallization rate of PTT was measured by the polarized light microscopy. Figure 8 shows the polarized light micrographs of PTT isothermally crystallized from the melt at 204°C for various time intervals. It is clear that these crystals grow as spherulite morphology. The positive Maltese cross pattern is evident, indicating along or perpendicular to orientation of the crystalline molecular axis with respect to the spherulitic radius.^{22,23} The dimensions of the crystallites are very sensitive to crystallization temperature and time. Figure 9 gives plots of the PTT spherulite radius as a function of time at different crystallization temperatures. It is obvious that the growth rate of the spherulite is sensitive to crystallization temperature and crystallization time. In Figure 9, these solid lines represent the best least squares fit to the data. It is clearly shown that there is a linear increase in the radius with time until the spherulites impinge on each other. It was also observed that the induction time for nucleation becomes longer at higher crystallization temperatures. From the slope of the straight lines, the spherulite growth rate of the PTT can be estimated. Figure 10 shows the spherulite growth rate of the pure PTT and some of its blends. It can be seen that the spherulite growth rate of PTT decreases dramatically as the crystallization temperature is increased. For the PTT/PEI = 90/10 blend, there is a significantly depression in spherulite growth rate relative to that of the pure PTT. For a higher PEI such as the blend of PTT/PEI = 80/20, the spherulite growth rate becomes very slow over the whole range of crystallization temperatures measured. Combining the results from DSC and polarized light mi-

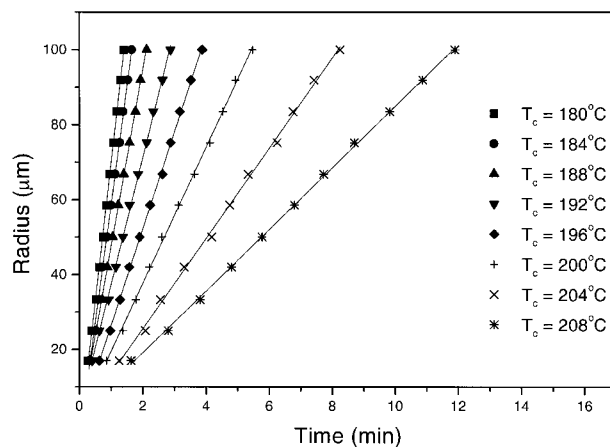


Figure 9 Radius of PTT spherulite vs. crystallization time under different crystallization temperatures.

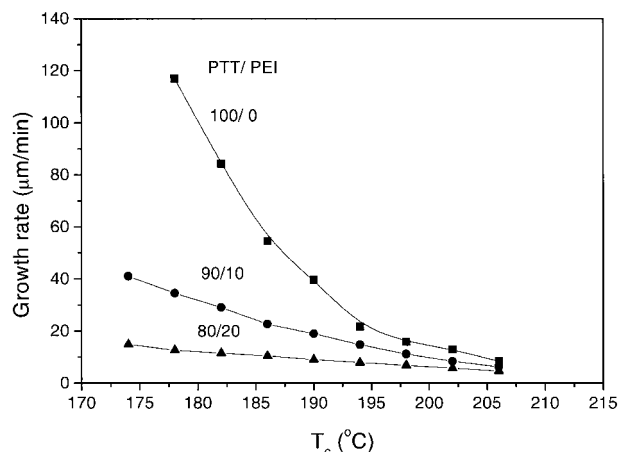


Figure 10 Spherulite growth rate as a function of crystallization temperature for PTT and PTT/PEI blends.

crosscopy measurements, it gives the same trend that the PTT crystallization is severely restricted at higher PEI content. Higher T_g of the blend and higher viscosity result in almost total inhibition of PTT crystallization on those blends containing greater than 50% PEI.

CONCLUSIONS

In this study, the miscibility, melting, and crystallization behaviors of solution-blended PTT/PEI blends have been investigated. From TGA analyses, these PTT/PEI blends show improved thermal stability than the pure PTT. From DSC measurements, PTT/PEI blends are miscible over the whole composition range based on single T_g of these blends. The relationship between T_g and composition in these blends can be fit well by the Golden-Taylor equation. Increasing the PEI content lowers the melting temperature and increases the cold-crystallization temperature. This result further demonstrates that PTT and PEI are miscible, and the presence of PEI in the blends retards or even inhibits the crystallization of PTT depending on PEI content. PTT and its blends show multiple melting endotherms, similar to other semicrystalline polymers such as PET and PEEK. The presence of PEI depresses the recrystallization of PTT during the DSC heating scan. The relative height of the highest endotherm to the middle endotherm decreases with increasing PEI component. Both crystallization temperature and enthalpy of crystallization exotherm decrease with increasing cooling rate and

the content of PEI in the blend. The retardation or inhibition of PTT component crystallization can be attributed to: (1) higher T_g of the blend with increasing PEI content results in lower PTT chain mobility; (2) high melt viscosity of the amorphous PEI component in the blend tends to decrease the rate of PTT segments diffusing to the crystallite-melting interface and leads to lower crystallization growth rate. From above studies, it can be concluded that blending of the semicrystalline PTT with the amorphous PEI results in a miscible blend and the PTT crystallization behavior is altered significantly.

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