Melting and Crystallization Behaviors of Compatibilized Poly(trimethylene terephthalate)/Acrylonitrile–Butadiene–Styrene Blends

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ABSTRACT: The melting and crystallization behaviors of poly(trimethylene terephthalate) (PTT)/acrylonitrile–butadiene–styrene (ABS) blends were investigated with and without epoxy or styrene–butadiene–maleic anhydride copolymer (SBM) as a reactive compatibilizer. The existence of two separate composition-dependent glass-transition temperatures (T_g's) indicated that PTT was partially miscible with ABS over the entire composition range. The melting temperature of the PTT phase in the blends was also composition dependent and shifted to lower temperatures with increasing ABS content. Both the cold crystallization temperature and T_g of the PTT phase moved to higher temperatures in the presence of compatibilizers, which indicated their compatibilization effects on the blends. A crystallization exotherm of the PTT phase was noticed for all of the PTT/ABS blends. The crystallization behaviors were completely different at low and high ABS contents. When ABS was 0–50 wt %, the crystallization process of PTT shifted slightly to higher temperatures as the ABS content was increased. When ABS was 60 wt % or greater, PTT showed fractionated crystallization. The effects of both the epoxy and SBM compatibilizers on the crystallization of PTT were content dependent. At a lower contents of 1–3 wt % epoxy or 1 wt % SBM, the crystallization was retarded, whereas at a higher content of 5 wt %, the crystallization was accelerated. The crystallization kinetics were analyzed with a modified Avrami equation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3334–3345, 2008

Key words: blends; crystallization; poly(trimethylene terephthalate)

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is a newly commercialized crystalline polymer with growing applications in fibers, films, and engineering plastics.[1–3] This polymer was reported to have outstanding tensile elastic recovery, good chemical resistance, a relative low melting temperature (T_m), and a rapid crystallization rate.[4] As an engineering thermoplastic, it was found to have mechanical properties similar to those of poly(ethylene terephthalate) (PET), whereas its processing characteristics were similar to those of poly(butylene terephthalate) (PBT). Thus, it combines some of the advantages of PET and PBT.[4]

In addition, PTT possesses all of the advantages of thermoplastic polyesters, such as their dimensional stability, solvent resistance, and abrasion resistance and can be used under moist conditions where nylon cannot be used. The performance of glass-fiber-reinforced PTT was also found to be better than that of reinforced PET or PBT, and some of its mechanical properties are comparable to those of glass-fiber-reinforced nylon.[2] Since its commercialization in 1998, PTT has been widely studied, especially with regard to its fiber properties,[5–8] structure formation,[1,9–11] crystal structure,[12,13] and thermal and crystallization properties.[14–19]

However, the low heat distortion temperature, low melt viscosity, poor optical properties, and pronounced brittleness of unreinforced PTT at low temperatures have restricted its use as a desirable engineering plastic. Some of these deficiencies could be improved by the development of PTT composites or blends with suitable polymers in which it retains its excellent properties. Polymer blending is a straightforward, versatile, and relatively inexpensive method of creating a new polymer material that has the desirable properties of all of the constituent com-

ponents. PTT blends are expected to possess a wide range of features that will broaden the applications of the homopolymer. Recently, a considerable amount of research work pertinent to PTT blends has been reported,[20–31] Guerrica-Echevarría et al.[21] found that the toughness of PTT was improved when it was blended with poly(ethylene–octene). Run et al.[22] and Krutphun and Supaphol[23] reported that PTT was miscible with poly(ethylene naphthalate) in the amorphous phase and that the variation in the glass-transition temperature (T_g) with the blend composition fit the Gordon–Taylor equation well. The correlation of the morphology and rheological response of PTT/m-(linear low-density polyethylene) blends was investigated by Jafari et al.[24] Compatibilization studies of PTT/ethylene–propylene–diene copolymer,[25] PTT/polystyrene,[26] and PTT/polypropylene (PP)[27] blends have been recently reported. The miscibility and melting and crystallization behaviors of PTT/poly(ether imide) (PEI),[28] PTT/ poly(ethylene naphthalate),[29] and PTT/polycarbonate (PC)[30] blends have also been reported.

Acrylonitrile–butadiene–styrene (ABS), an extensively used commercial polymer, is associated with good processability, dimensional stability, and higher impact strengths at lower temperatures. ABS is a feasible choice for blending with PTT because of their potential combination of good impact strength, modulus, and heat, chemical, and abrasion resistance. However, until now, no commercial blend products based on PTT and ABS, or even fundamental studies of such blends, have been reported. Because the tailor-made properties of the final blend products depend on the miscibility between the components and the phase structures of the blends, compatibilization is required to obtain a blend with the desired properties. PTT has carboxyl and/or hydroxyl terminal groups that can react with epoxide, amine, anhydride, and acrylic acid functional groups during melt blending, whereas ABS consists of poly(styrene acrylonitrile (SAN) plastic and polybutadien (PB) rubber phases without any active functional groups. The most common compatibilization strategy is to incorporate a functional polymer that is capable of reacting with the carboxylic acid and/or hydroxyl terminal groups of PTT and that is also miscible with ABS. Accordingly, a glycidyl end-capped epoxy (poly[(bisphenol A)-co-epichlorohydrin]) and a styrene–butadiene–maleic anhydride copolymer (SBM) can act as compatibilizers for PTT/ABS blends.

The polymer blending process has a great impact on the melting and crystallization behaviors of the crystalline components;[19,31–33] moreover, the melting and crystallization behaviors of a crystalline polymer in the blend is an important aspect of the characterization of the physical properties of the blend. In PTT/ABS blends, the presence of ABS may accelerate, interfere, or even suppress the crystallization process of the PTT phase, which is dependent on the degree of their compatibility, the composition, and the blend rheology. Meanwhile, the crystallization process dramatically affects the crystal structure, the physical and mechanical properties of the blend, and the resultant blend's supermolecular structures established during solidification. To understand and control the crystallization process and to obtain the desired morphology and properties, the investigation of the crystallization behavior of PTT in PTT/ABS blends under nonisothermal conditions and its melting behavior are of great significance for the technological optimization and manufacture of high-performance polymeric materials. In this study, with epoxy and SBM selected as compatibilizers, the melting and crystallization behaviors of PTT/ABS blends were investigated with and without the compatibilizers.

EXPERIMENTAL

Materials

Clear PTT, with the trade name Corterra CP509201, was supplied by the Shell Chemical Co. (West Virginia). The polymer had an intrinsic viscosity of 0.92 dL/g, measured in a 60 : 40 mixture of phenol and tetrachloroethane at 30°C. ABS, with the trade name Polylac PA-747S (extrusion grade) was purchased from Chi Mei Corp. (Tainan, Taiwan). SBM, with the trade name MPC 1545R, was purchased from Shanghai Sunny New Technology Development Co., Ltd. (Shanghai, China). The maleic anhydride unit content was 7 wt %. Poly [(bisphenol A)-co-epichlorohydrin], with the trade name E-03 (609), a glycidyl end-capped epoxy resin with an epoxy equivalent weight of about 3000 g/equiv, was supplied by the Institute of Tianjin Synthetic Materials (Nanjing Giant, Nanjing, China). Before melt processing, PTT was dried at 140°C for 12 h in a vacuum oven to minimize the hydrolytic degradation of the melts. ABS, the epoxy, and SBM were dried at 85°C for 2 h in a vacuum oven. All of the components were thoroughly mixed before extrusion.

Blend preparation

The melt blending of the dried PTT and ABS with different compositions was carried out with a 35-mm twin-screw corotating extruder (Nanjing Giant, Nanjing, China). The barrel temperature ranged from 245 to 255°C, and the screw speed was 144 rpm. Samples for differential scanning calorimetry (DSC) analysis were obtained from the cooled extrudates after melt blending.

DSC measurements

DSC measurements were carried out using a Netzsch differential scanning calorimeter (model

DSC-204, Germany). The temperature was calibrated with an indium standard. The measurements were performed under a high-purity nitrogen atmosphere to minimize the possibility of moisture regain and thermooxidative degradation. To avoid uneven thermal conduction through the samples, the sample weights were maintained at 7.5 ± 0.5 mg. The samples obtained at the same cooling stage during the extrusion process sealed in aluminum pans were heated from 20 to 270°C at a heating rate of 10°C/min and kept at 270°C for 5 min to eliminate thermal and mechanical histories; then, the samples were cooled to 20°C at a cooling rate (R) of 10°C/min. The thermograms were recorded as a function of temperature.

Scanning electron microscopy (SEM) and microscopy sample preparation

The extruded bars were fractured in liquid nitrogen perpendicular to the direction of flow. The fracture surface of the blend was etched with toluene at 80°C to remove the ABS phase, and then, the rinsed and dried sample was gold-coated for SEM (JEOL JSM-6700F, Japan) examination. The sample for microscopy were prepared with a hot stage, and the morphology was observed with an Olympus BX-51 microscope.

Characterization of the nonisothermal crystallization kinetics of PTT in the PTT/ABS blends

Generally, the isothermal crystallization kinetics of a polymer are analyzed with the Avrami equation.[34,35] However, the theoretical analysis of a nonisothermal crystallization is more complicated. Mandelkern[36] suggested that the primary stage of a nonisothermal crystallization could still be described by the Avrami equation, as illustrated in eq. (1):

$$1 - X(t) = \exp(Z_t t^n) \tag{1}$$

$$\log\{-\ln[1 - X(t)]\} = \log Z_t + n \log t \tag{2}$$

where Z_t is the growth rate constant; n is the Avrami exponent, which is dependent on the nucleation and growth mechanisms; and $X(t)$ is the relative degree of crystallinity at time t and is obtained from the area of the DSC exotherm at time t divided by the total final area under the exotherm, as shown in eq. (3):

$$X(t) = \frac{\int_{T_i}^{T_c}(dH/dT)dT}{\int_{T_i}^{T_\infty}(dH/dT)dT} \tag{3}$$

where H and T are crystallization enthalpy and crystallization temperature respectively, and T_c is the crystallization temperature at time t, T_i is the initial crystallization temperature, and T_∞ is the temperature at which the crystallization process is completed.
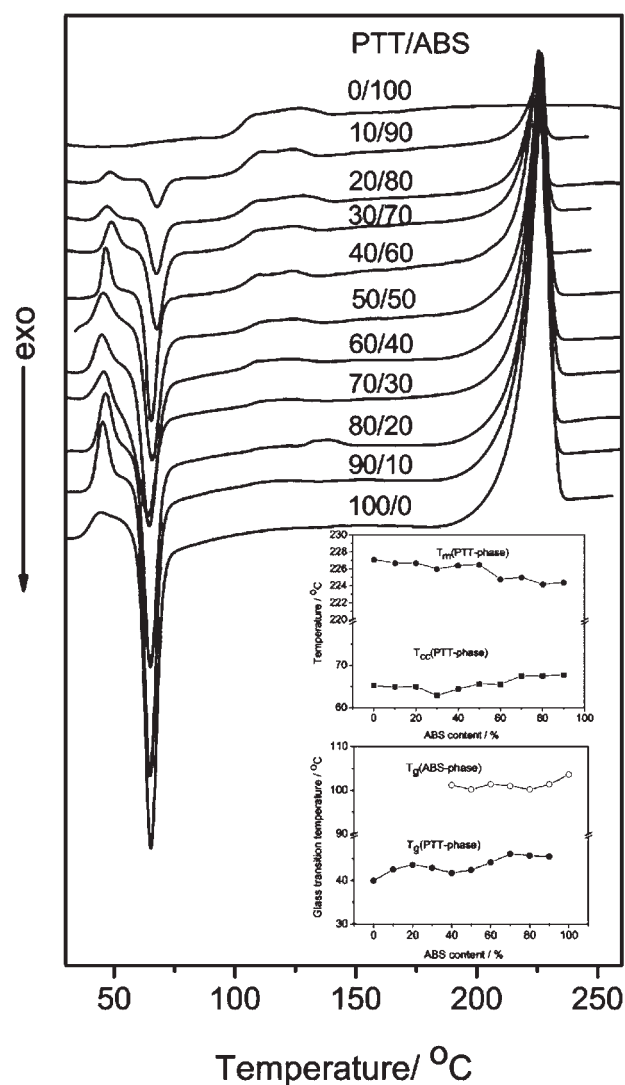
Figure 1 DSC heating thermograms of the PTT/ABS blends with various compositions (DSC heating rate = 10°C/min). The inserted figures show the changes in T_{cc} (PTT phase), T_m (PTT phase), T_g (PTT phase), and T_g (ABS phase) with blend composition.

In nonisothermal crystallization, Jeziorny[37] suggested that Z_t should be corrected by R as follows:

$$\log Z_c = (\log Z_t)/R \tag{4}$$

where Z_c is the kinetic parameter of the nonisothermal crystallization.

RESULTS AND DISCUSSION

Melting behavior of the PTT/ABS blends

Figure 1 shows the DSC heating scans for the PTT/ABS blends. Two T_g's were observed, which indicated that the blends were phase-separated in the amorphous phase. The lower temperature transitions observed between 40.7 and 46.1°C were attributed to

the T_g's of the PTT amorphous phase. The higher temperature transitions observed from 103.6 to 100.2°C were the T_g's of the SAN transitions in the ABS matrix. The dependences of the two T_g's on the blend composition are shown as an insert in Figure 1. The variations of the two T_g's were composition dependent. When the ABS content was increased from 0 to 70 wt %, the T_g (PTT phase) shifted from 40.7 to 46.1°C and then remained at about 46°C when the ABS content was further increased above 70 wt %. In contrast, T_g (ABS phase) decreased 2.3°C after the addition of 10 wt % of PTT and then remained unchanged with further PTT addition. These results illustrate typical behaviors of a partially miscible system[32,38,39] and indicate that PTT was partially miscible with ABS and that the miscibility increased slightly with ABS content. If the empirical Fox equation[40] is assumed to be applicable to the PTT/ABS blends, the T_g changes imply that the solubility of ABS in the PTT phase was greater than that of PTT in the ABS phase.

The variations in the T_m and cold crystallization temperature (T_{cc}) of PTT as a function of the blend compositions are shown in another insert in Figure 1. The T_m value shifted to lower temperatures with increasing ABS content. In general, for a blend exhibiting some phase mixing, the presence of a second partially solubilized polymer will cause T_m to decrease because of the reduction in the chemical potential. This behavior is usually observed in the case of miscible or partially miscible blends.[28,30,39,41,42] Accordingly, the variation of T_m indicated that the solubility of ABS in the PTT phase slightly increased with increasing ABS content. On the other hand, it also implied that PTT and ABS were partially miscible. In contrast, the T_{cc} value shifted slightly to higher temperatures as the ABS
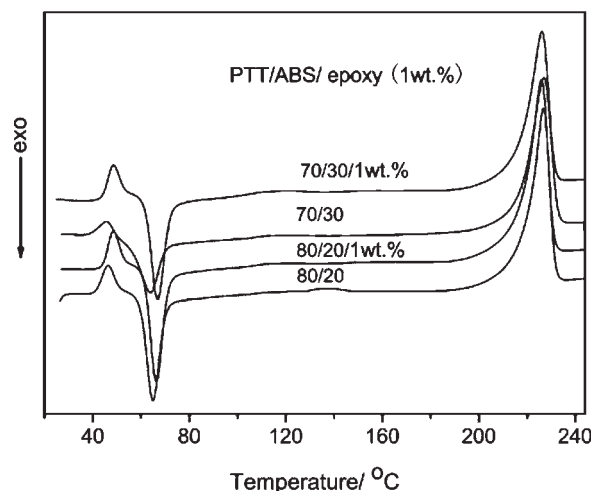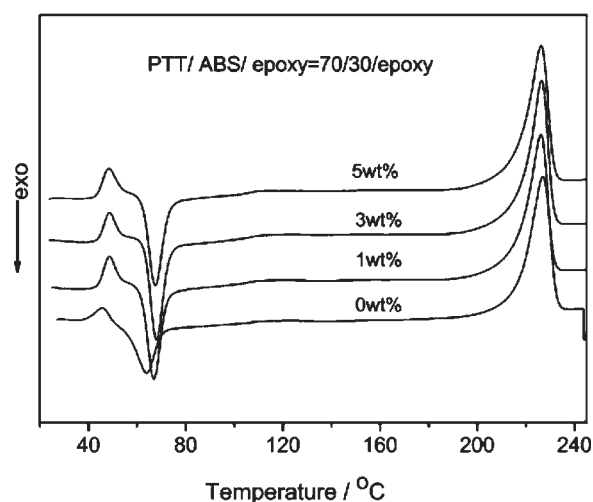

Figure 3 Effects of the epoxy content on the heating process of the PTT/ABS blends (DSC heating rate = 10°C/min).

content was increased, which indicated that a much higher activation energy was needed for the organization of the neighboring PTT segments because of the interference of the ABS segments.

Influences of the compatibilizers on the melting behavior of the PTT/ABS blends

Figure 2 shows the effects of 1 wt % epoxy on the melting behavior of the PTT/ABS blends. It was clear that both the T_g and T_{cc} values of the PTT phase shifted to higher temperatures in the presence of the epoxy. This indicated that excess energy was needed to initiate the movements or regular arrangement of the PTT segments because of the epoxy's compatibilization effect. However, T_m showed no discernable changes in the compatibilized and uncompatibilized blends. These results are consistent with those obtained for the effect of PTT in PTT/PC blends compatibilized by epoxy.[32] Figure 3 shows the influence of the epoxy content on the DSC heating thermograms of the PTT/ABS blends. The T_{cc}'s of the compatibilized blends were higher than those of the uncompatibilized blends. As the epoxy content increased from 1 to 3 wt %, T_{cc} shifted to a higher temperature and then showed a slight decrease at an epoxy content of 5 wt %. This implied that 5 wt % epoxy was an excessive dosage and that the part of it which did not function as a compatibilizer may have acted as a plasticizer and/or nucleation agent, which caused cold crystallization to occur relatively easily.

The influence of 3 wt % SBM on the melting behavior (Fig. 4) was similar to that of 1 wt % epoxy. Both the T_g and T_{cc} values of the PTT phase in the SBM compatibilized blends shifted to higher temper-

Figure 2 Effect of 1 wt % epoxy on the heating process of the PTT/ABS blends (DSC heating rate = 10°C/min).
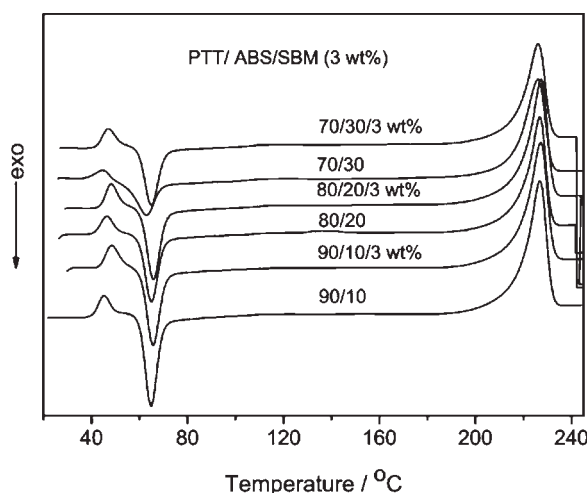
Figure 4 Effect of SBM on the heating process of the PTT/ABS blends (DSC heating rate = 10°C/min).

atures compared to the uncompatibilized blends, which indicated the compatibilization effect of SBM on the blends. However, the changes in both the T_g and T_{cc} values (Fig. 5) indicated that the compatibilization effect of SBM did not show obvious dependence on its content (1–5 wt %), as did that of the epoxy.

Crystallization behavior of the PTT/ABS blends

Generally, for a polymer blend containing a crystallizable component, the second component may influence the crystallizable polymer's crystallization in four ways: (1) no effect on the crystallization rate or morphology, (2) acceleration the crystallization process, (3) retardation of crystallization with or without a change in morphology and the prevention of crystallization at high content, and (4) induction of fractionated crystallization, especially at high loadings.
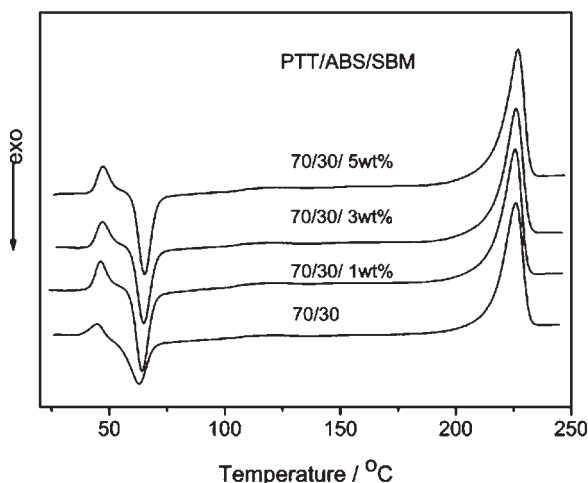

Figure 5 Effect of SBM content on the heating process of the PTT/ABS blends (DSC heating rate = 10°C/min).
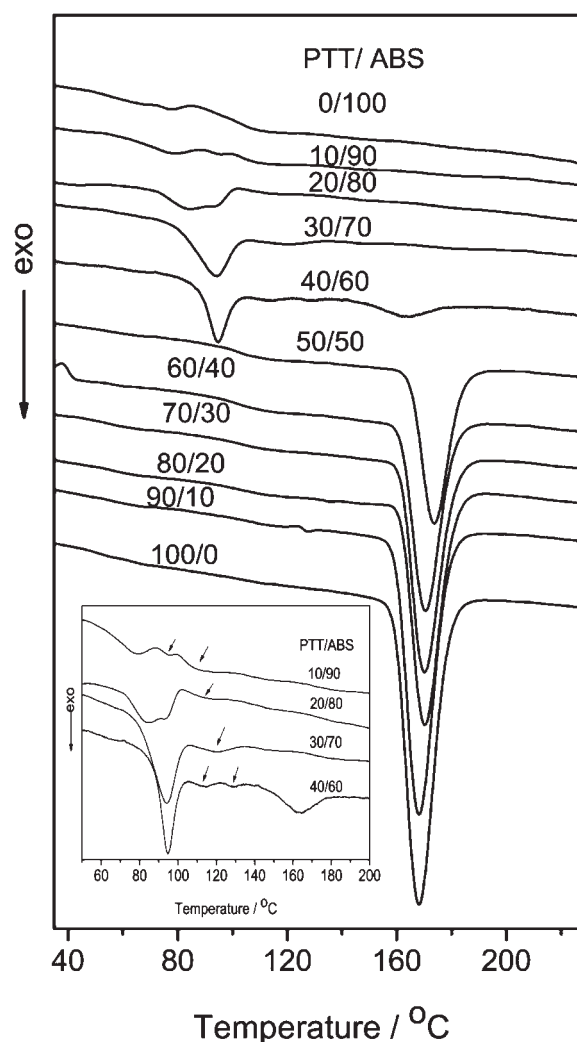

Figure 6 DSC cooling traces for the PTT/ABS blends. The insert shows the fractionated crystallization behavior of the PTT phase ($R = 10$°C/min)

Figure 6 shows the crystallization behavior of PTT in the PTT/ABS blends. Obviously, PTT exhibited completely different crystallization behaviors at low and high ABS contents. A content of 60 wt % ABS was a dividing or watershed content. When ABS was 0–50 wt %, the crystallization process of PTT shifted slightly to higher temperatures, whereas the crystallization enthalpy fell considerably as the ABS content increased (Fig. 7). The former indicated the acceleration effect of ABS on PTT's crystallization, and the latter was mainly due to the lower PTT content involved in the blends. This crystallization behavior was similar to PTT's crystallization in PTT/PP blends when PTT is a matrix phase.[43] Generally, the presence of one component may influence the other component's crystallization process in three ways. The first is the nucleation effect, which lowers the nucleation energy and is enhanced by an increase in the interfacial area. The second is the influence on nuclei growth by dilution of the concen-
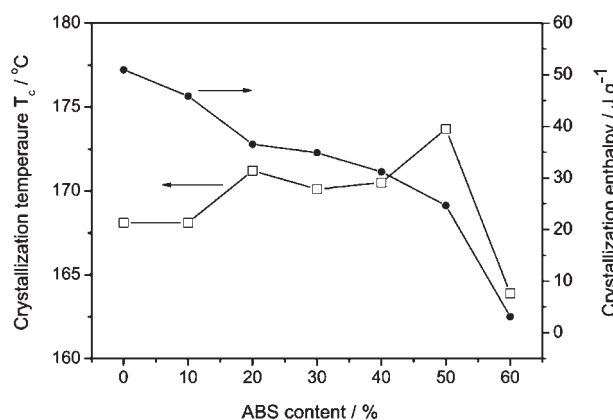
Figure 7 Effects of ABS content on T_c and the crystallization enthalpy of the PTT phase.

tration of the crystallizable component near the growth fronts. The third is the interference of the component chain segments incorporating into the growing crystal lattice, which increases the system's overall free energy. For different polymer pairs, the crystallization responses of the three effects are different, and the observed crystallization behavior is a result of the three effects' competition and a predominance reflection. At the crystallization temperature of PTT ($\sim 170°C$) in the PTT/ABS blends, ABS was in melting or semimelting state. The three effects were speculated to be at work, especially at the interface area. Figure 6 indicates that the nucleation effect of ABS was predominant when PTT ≥ 50 wt %, which enhanced PTT's crystallization; this enhancement was more pronounced with increasing ABS content.

However, the crystallization exhibited a completely different behavior when the ABS content was 60 wt %. The normal crystallization exotherm moved to a much lower temperature with diminished intensity and became broad, which indicated that a classical crystallization retardation occurred; simultaneously, a well-developed lower temperature exotherm with a peak temperature at about $95°C$ coexisted with two small indistinctive exotherms (arrow marked in the insert figure in Fig. 6) with peak temperatures at about 110 and $130°C$, respectively, appeared. This is a phenomenon of fractionated crystallization,[44,45] which is usually observed in immiscible blends.[44,46–48] Fractionated crystallization has been shown to be related to a fine phase morphology,[44] in which the total number of dispersed crystallizable droplets exceeds the number of heterogeneities with the lowest activation energy, normally active in bulk crystallization. Thus, the smaller droplets, due to a lack of such heterogeneities, will show crystallization at much higher degrees of supercooling nucleated by heterogeneities with the second to the lowest activation energy or will even show homogeneous crystallization where the polymer chains

have to nucleate on their own. Therefore, multiple crystallization peaks can be considered to reflect the efficiency spectrum of the several nucleating heterogeneous nuclei available in the dispersed crystallizable polymer phase and possibly also crystallization triggered by homogeneous nucleation.[44]

In immiscible or poorly miscible blends, the interfacial tension is high and the interface is sharp, whereas the interfacial layer is thin. If the interface wets well with the crystalline matrix, it will result in heterogeneous nucleation and may accelerate the crystallization process, when PTT was 50 wt % or greater. However, when the crystallizable polymer is a minor dispersed phase in the matrix, such as when the PTT content was lower than 40 wt %, a series of crystallization exotherms are observed at much lower temperatures instead of crystallization at their bulk crystallization temperature; furthermore, these lower temperature exotherms shifted to lower temperatures as the ABS content increased, which indicated that the much finer dispersion led to crystallizations with much higher supercooling degrees. This is consistent with other reports.[44–48] From this point of view, the prediction of fractionated crystallization can be made on the basis of blend-phase morphology and vice versa. Everaert et al.[44] demonstrated that the onset composition of fractionated crystallization relates to the center of the phase-inversion region. Accordingly, the crystallization behavior of PTT in the PTT/ABS blends implied that 40 : 60 PTT/ABS was in the phase-inversion region with the phase-inversion morphology. To verify this, the morphologies of the PTT/ABS blends were investigated with SEM and microscopy, as shown in Figure 8. Figure 8(a) is the SEM image of the 50 : 50 PTT/ABS blend. We selectively removed the ABS phase of the blend fracture surface by hot toluene etching without affecting the PTT phase. Some of the dispersed ABS particles began to coalesce and existed as connected spheres, which indicated that the blend began to phase inverse at 50 wt % ABS content. For the 40 : 60 and 30:70 compositions, the hot toluene etching method could not be used to prepare SEM samples because the samples collapsed when the ABS phase was removed. Therefore, the morphologies of the blends were studied by phase contrast microscopy, as shown in Figure 8(b,c). Figure 8(b) shows that some of the PTT domains were still large sized instead of existing as isolated spherical particles, which indicated that the phase inversion had not finished and that the 40 : 60 composition was in the phase-inversion region. When the PTT content was 30 wt %, the large PTT domains disappeared, and only the isolated PTT spheres were noticed. Corresponding with the phase morphology of the 30 : 70 composition, only the fractionated crystallizations exotherms were observed in the DSC thermograms.
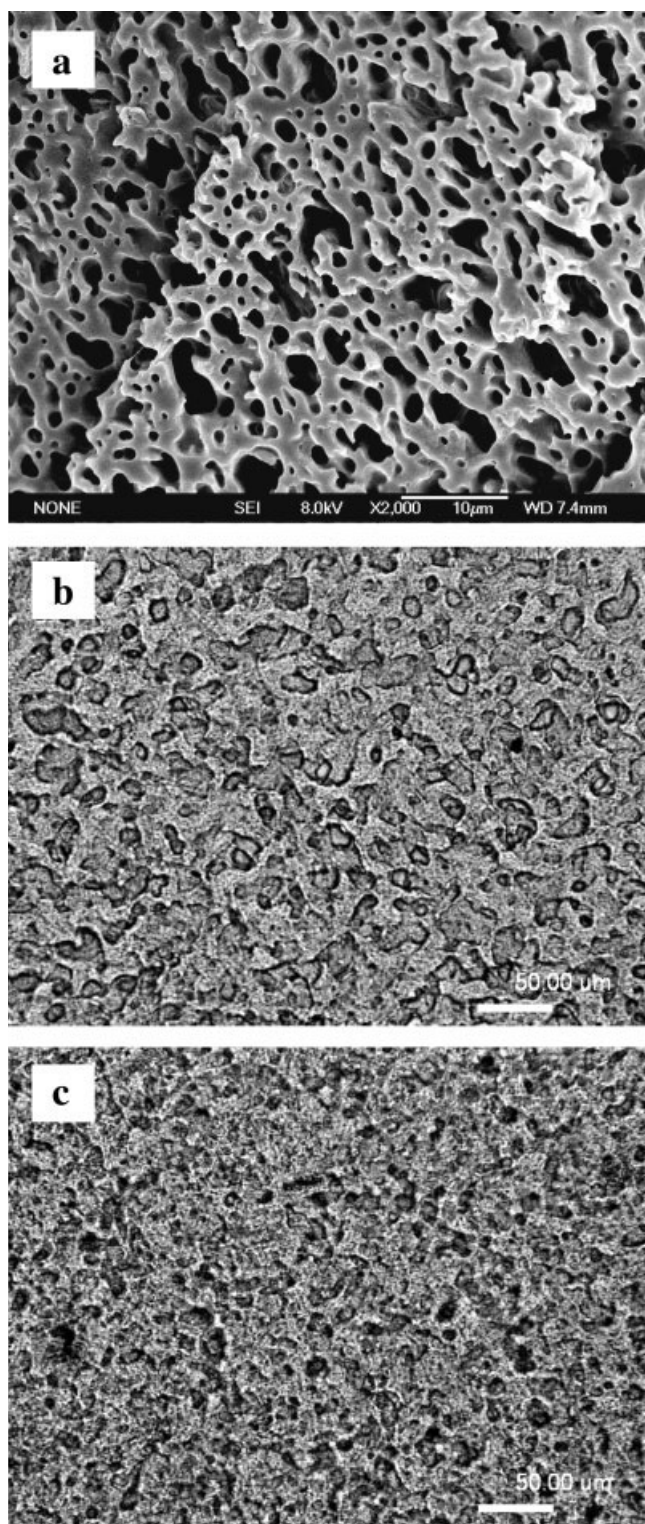
Figure 8 Phase morphologies of the PTT/ABS blends: (a) SEM image with the ABS phase etched out by toluene and (b,c) phase contrast images.

Considering both the phase morphology and fractionated crystallization developments with the blend composition, we confirmed that the fractionated crystallization was related to presence of the finely dis-

persed PTT phase. In the phase-inversion region, the PTT chains in the large-size domains may have shown crystallization near to the bulk crystallization temperature even though the crystallization was severely interfered with, whereas the chains in the finely dispersed PTT phases showed crystallization at much higher supercooling degrees.

From the crystallization behavior of PTT in the PTT/ABS blends, it seemed that the crystallization behavior of PTT in the PTT/ABS blends depended strongly on the phase morphology, and it played a key role with respect to the fractionated crystallization, but our studies on the crystallization behaviors of PTT in the PTT/PP,[43] PTT/PC,[19] and PTT/ABS indicated that the crystallization of PTT in the blends depended on its crystallization nature, and it was influenced by the phase morphology, component, processing equipment, composition, and so on. When PTT was a matrix phase, its crystallization was accelerated by the presence of ABS or PP while retarded by PC; the higher content of the other component was, the much more severe the influence on PTT's crystallization was. During the phase-inversion region, PTT showed a retarded bulk crystallization exotherm coexisting with the crystallization exotherms (PTT/ABS, PTT/PP) at high supercooling degrees. A possible reason for this bulk crystallization retardation is that the morphology of the phase-inversion region, with a large interface area, was available for both nucleation and interference with PTT's crystallization, and the DSC results indicated that its negative contribution to the crystallization rate exceeds its positive contribution. When PTT is as a dispersed phase, it showed fractionated crystallization at much lower temperatures (PTT/ABS, PTT/PP), or it could be prevented completely (PTT/PC) by the other component. Compared with ABS and PP, the interference of PC on the crystallization process of PTT was the most severe. We confirmed that PTT did not show crystallization when PC $\geq$ 40 wt % in the PTT/PC blends, although the crystallization ability of PTT in blends was influenced by the processing equipment and the processing time to some extent (PTT/ABS and PTT/PP were processed by a twin-screw extruder, whereas PTT/PC was prepared by a Haake instrument). When PTT was a dispersed phase, its crystallization ability was low, and this was mainly because of the active nucleus shortage. The finer the dispersion was, the greater was the lack of active nucleus with lower activation energy.

Effects of the epoxy or SBM compatibilizer on the crystallization behavior of the PTT/ABS blends

Figure 9 shows the effects of the epoxy on the crystallization behavior of PTT in the PTT/ABS blends. With 1 wt % epoxy addition, the crystallization exo-
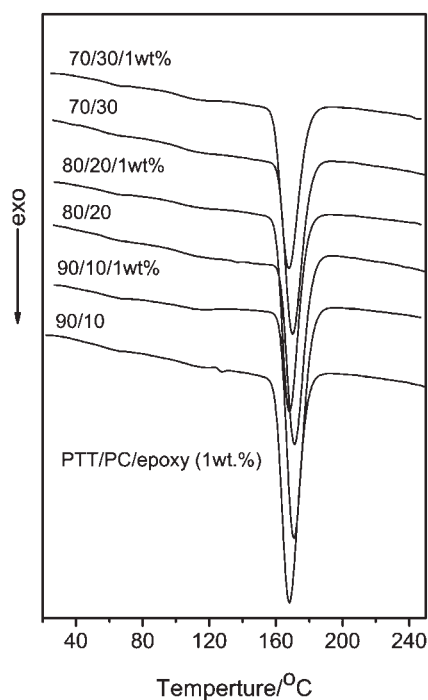
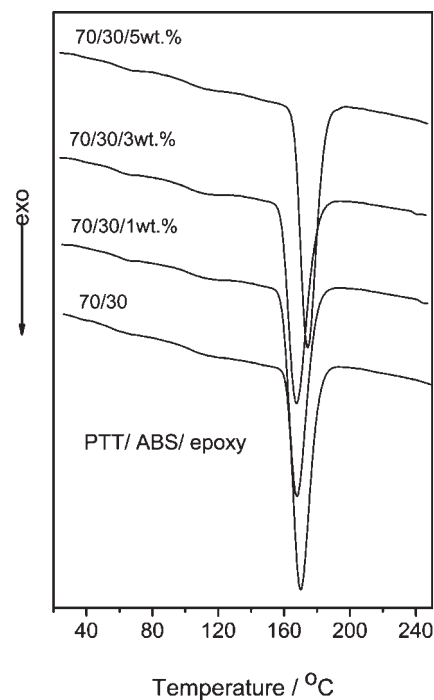**Figure 9** Effects of the epoxy on the crystallization behaviors of the PTT/ABS blends (DSC $R = 10°C/min$).

Figure 10 Effects of the epoxy content on the crystallization behaviors of the PTT/ABS blends (DSC $R = 10°C/min$).

therms of the 80 : 20 and 70 : 30 PTT/ABS blends moved to lower temperatures, whereas the crystallization exotherm of the 90 : 10 PTT/ABS blend shifted to a higher temperature in comparison with the corresponding uncompatibilized blends. This can be explained by the compatibilization effect of the epoxy on the blends. The reactive products formed during melt processing between the epoxy and PTT, which preferentially resided at the polymer–polymer interfaces, improved the miscibility and adherence among microdomains and, thus, resulted in excess energy that should have been dissipated when PTT crystallized. On the other hand, the reactive products, which did not function as compatibilizers, probably served as nucleation agents. The DSC results indicated that the epoxy in the 80 : 20 and 70 : 30 PTT/ABS blends mainly functioned as a compatibilizer, whereas it served as a nucleation agent, accelerating the crystallization of PTT, in the 90 : 10 PTT/ABS blend, and this enhancement covered the crystallization retardation effect of its compatibilization on the blends.

Figure 10 shows the effect of the epoxy content on the crystallization of the blends. As the epoxy content increased from 0 to 3 wt %, the crystallization process of PTT shifted slightly to lower temperatures. However, the crystallization moved to a higher temperature for 5 wt % epoxy, which indicated that the part of the epoxy that was free of compatibilization effect might have acted as a nucleation agent and accelerated PTT's crystallization.

These results are the same as the effect of the epoxy on the crystallization of PTT in PTT/PC blends.[19]

In contrast, SBM showed a lower effect on the crystallization of PTT in the PTT/ABS blends (Figs. 11 and 12). The addition of 3 wt % SBM did not
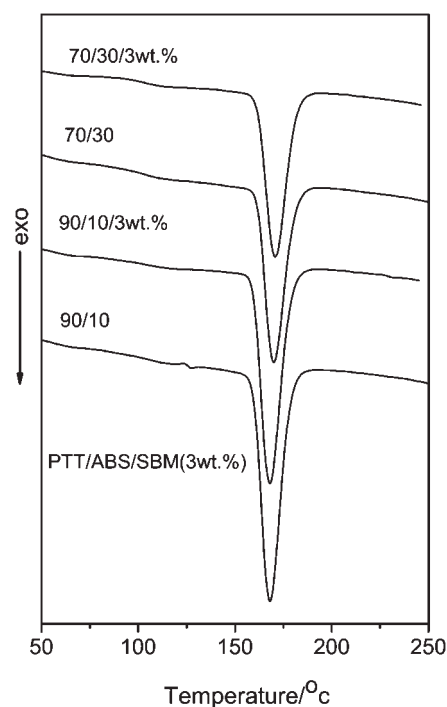

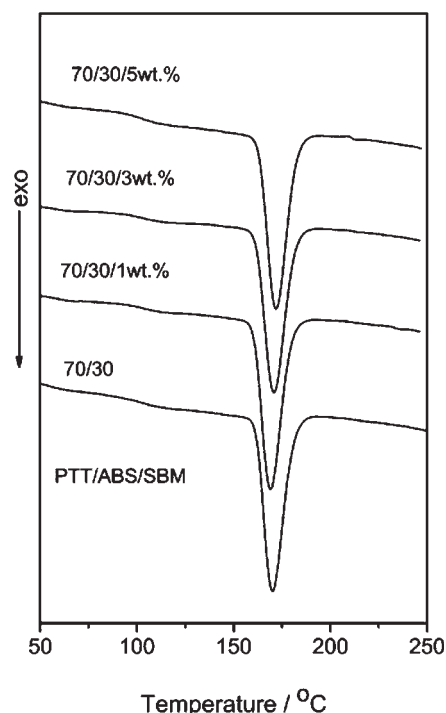**Figure 11** Effects of SBM on the crystallization behaviors of the PTT/ABS blends (DSC $R = 10°C/min$).

Figure 12 Effect of the SBM content on the crystallization behaviors of the PTT/ABS blends (DSC $R = 10°C/min$).

influence the crystallization temperatures of PTT in the 90:10 and 70:30 PTT/ABS blends. When the SBM content increased from 0 to 5 wt %, PTT's crystallization temperature changed in the sequence 170.1°C (0 wt %), 168.7°C (1 wt %), 170.7°C (3 wt %), and 172°C (5 wt %). The indicated that the effect of SBM on PTT's crystallization was content dependent. At a lower content of 1–3 wt % epoxy or 1 wt % SBM, the crystallization was retarded; whereas at a higher content of 5 wt %, the crystallization was accelerated.

Crystallization kinetics of PTT in the uncompatibilized PTT/ABS blends

Figure 13(a,b) shows PTT's relative crystallinities in the blends as a function of crystallization temperature and time, respectively. The addition of 10 wt % ABS did not show any effect on the crystallization process. However, 20 wt % ABS addition made the temperature to reach a given relative crystallinity shift to a higher temperature, and less crystallization time was needed compared with that of pure PTT. When ABS was 30–50 wt %, the relative crystallinity curves of the blends, compared with the crystallization of 100 wt % PTT, shifted to higher temperatures, and this confirmed the accelerating effect of ABS on PTT's crystallization. When ABS was 60 wt %, the temperature to reach a given relative crystallinity for bulk crystallization exotherm shifted considerably to

a lower temperature, and a longer crystallization time was needed. This could be attributed to two main factors. One was the lower crystal growth rate, which was due to the reduced mobility of the chains at higher supercooling degrees. The other was the nucleation problem at normal crystallization temperature, which was mentioned previously.

The insert in Figure 13(a,b) shows the changes in PTT's relative crystallinities for the crystallization exotherms at about 90°C. The crystallization time to reach a given crystallinity increased rapidly, and the crystallization rate decreased as ABS content was increased from 60 to 80 wt %.

n (Table I) suggested that the nucleation mechanism and the growth mode remained unchanged when the ABS content increased from 0 to 50 wt %. However, with 60 wt % ABS, n decreased to 2.43 for the bulk crystallization, whereas n was 3.22 for the lower temperature crystallization, which indicated that an athermal nucleation bulk crystallization coexisted with a thermal nucleation crystallization at lower temperatures. At 70 wt % ABS content, the lower temperature crystallization still maintained a
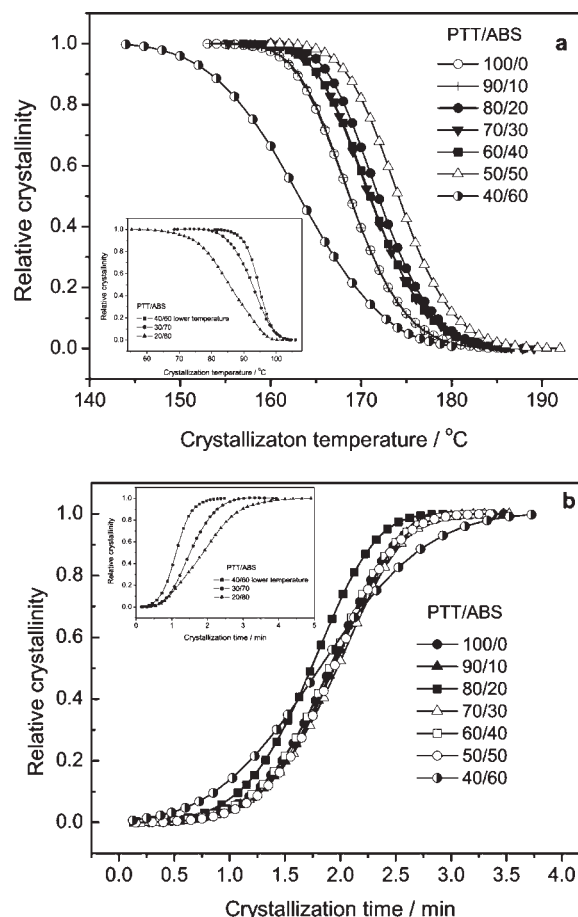

Figure 13 Relative crystallinity of the PTT phase as a function of (a) crystallization temperature and (b) crystallization time for the PTT/ABS blends.

TABLE I
Avrami Nonisothermal Crystallization Kinetics Parameters for the PTT/ABS Blends

PTT/ABS	Bulk crystallization		Low-temperature crystallization	
	n	Z_c	n	Z_c
100 : 0	4.11	0.74	—	—
90 : 10	4.04	0.74	—	—
80 : 20	3.56	0.79	—	—
70 : 30	3.63	0.74	—	—
60 : 40	3.83	0.75	—	—
50 : 50	3.90	0.73	—	—
40 : 60	2.43	0.83	3.25	0.93
30 : 70	—	—	3.44	0.83
20 : 80	—	—	2.69	0.81

thermal nucleation mechanism, but it changed to an athermal one when ABS was 80 wt %.

Crystallization kinetics of PTT in the compatibilized PTT/ABS blends

Figure 14 compares the development of the relative crystallinities of PTT in the blends with and without
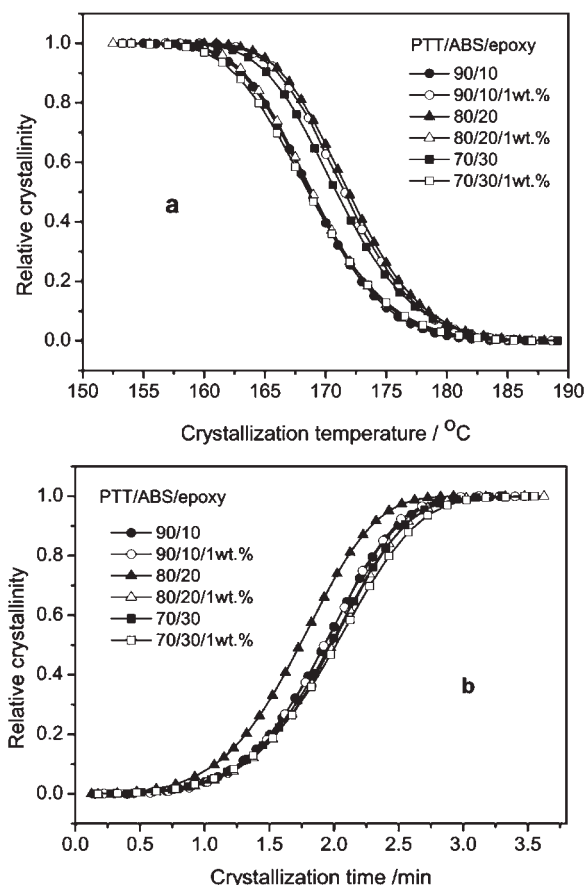

Figure 14 Relative crystallinity of the PTT phase as a function of (a) crystallization temperature and (b) crystallization time for the PTT/ABS blends with and without epoxy.
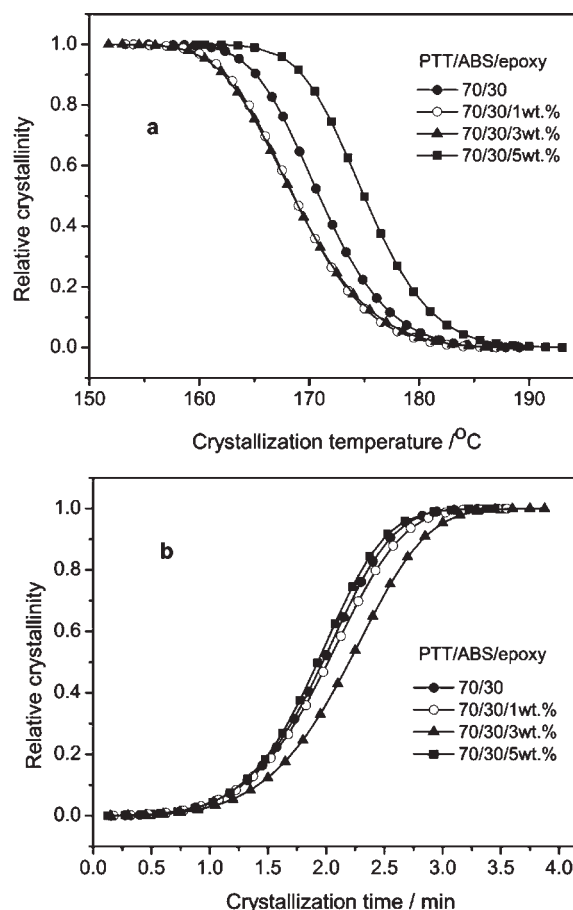

Figure 15 Effects of the epoxy content on the PTT phase crystallinity in PTT/ABS blends as a function of (a) crystallization temperature and (b) crystallization time.

epoxy. With 1 wt % epoxy addition, the crystallization proceeded at lower temperatures, and it took a little longer time to reach a given crystallinity for the 80 : 20 : 1 and 70 : 30 : 1 PTT/ABS/epoxy blends compared with the corresponding blends without compatibilizers. However, for the 90 : 10 : 1 PTT/ABS/epoxy blend, the crystallization temperature shifted to a higher temperature, whereas the crystallization time did not show any clear change in comparison with 90 : 10 PTT/ABS blend. These results demonstrated that the 1 wt % epoxy mainly functioned as a compatibilizer in the 80 : 20 and 70 : 30 PTT/ABS blends, whereas it acted mainly as a nucleation agent in the 90 : 10 PTT/ABS blend. Figure 15 shows that to reach a given crystallinity, the crystallization proceeded to lower temperatures when the epoxy content was 1 or 3 wt % and proceeded to a higher temperature for 5 wt % epoxy, compared with the corresponding uncompatibilized blend. This indicated that the compatibilization effect was predominant for 1–3 wt % epoxy content, whereas the nucleation effect was predominant for 5 wt % epoxy content. The n values (Table II) indi-

TABLE II
Avrami Nonisothermal Crystallization Kinetics Parameters for the PTT/ABS Blends with and Without Compatibilizers and Their DSC Peak Crystallization Temperatures

		T_c (°C)	n	Z_c
PTT/ABS	90 : 10	168.1	4.04	0.74
	80 : 20	171.2	3.56	0.79
	70 : 30	170.1	3.63	0.74
PTT/ABS/epoxy	90 : 10 : 1	170.8	4.59	0.72
	80 : 20 : 1	168.2	3.81	0.73
	70 : 30 : 1	167.8	3.62	0.74
	70 : 30 : 3	167.5	3.64	0.71
	70 : 30 : 5	174.2	3.78	0.75
PTT/ABS/SBM	90 : 10 : 3	168.0	4.14	0.74
	70 : 30 : 1	169.0	3.79	0.74
	70 : 30 : 3	170.8	3.80	0.75
	70 : 30 : 5	172.0	3.70	0.77

cated that the nucleation mechanism and the growth mode of PTT remained unchanged.

Figures 16 indicates that 3 wt % SBM addition caused little change in the crystallinity of PTT in the
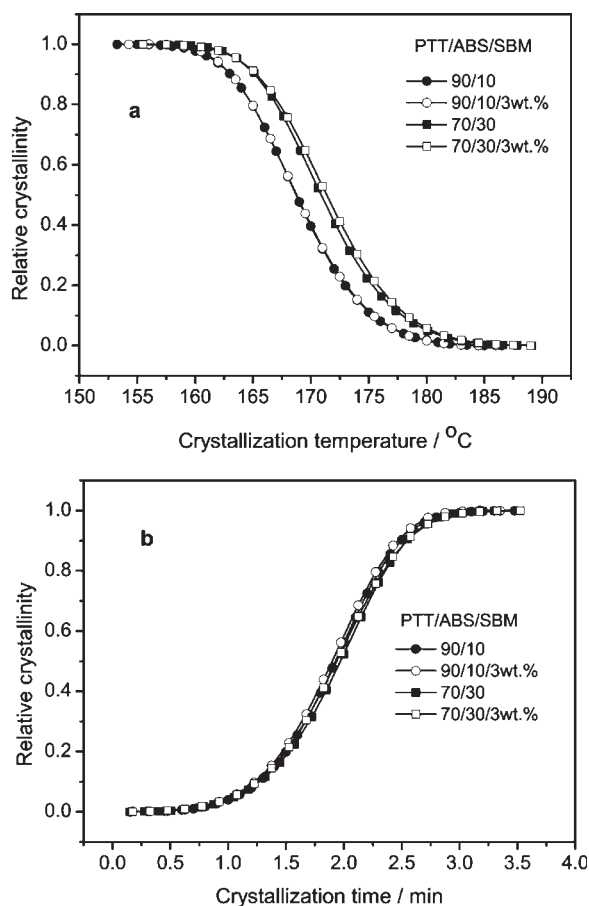

Figure 16 Relative crystallinity of the PTT phase as a function of (a) crystallization temperature and (b) crystallization time for the PTT/ABS blends with and without SBM.
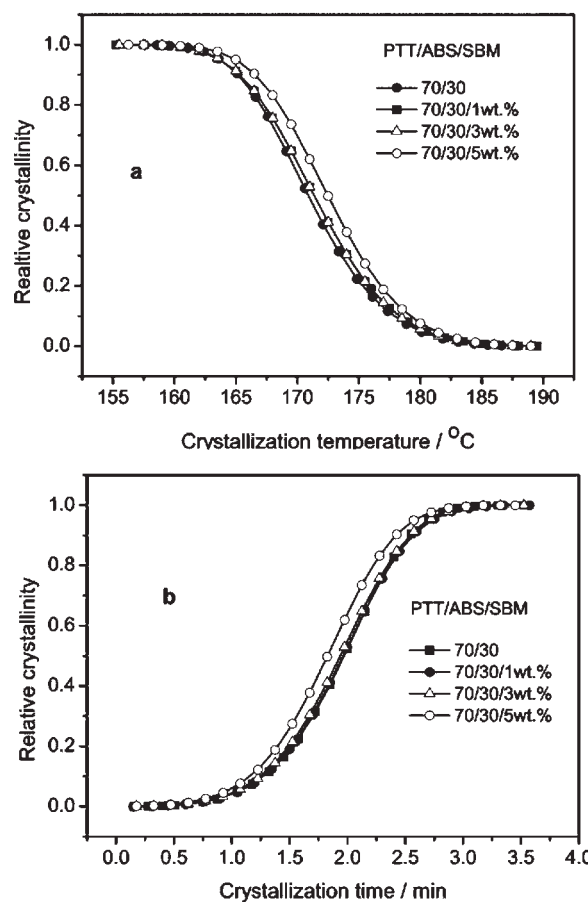
Figure 17 Effects of the SBM content on the PTT phase crystallinity in the PTT/ABS blends as a function of (a) crystallization temperature and (b) crystallization time.

SBM-compatibilized PTT/ABS blends. However, a 5 wt % SBM content made the crystallization temperature shift clearly to a higher temperature, and a slightly longer crystallization time was needed (Fig. 17). The n values (Table II) indicated that the nucleation mechanism and the growth mode remained unchanged.

CONCLUSIONS

The melting and crystallization behaviors of PTT/ABS blends were investigated with and without epoxy or SBM as a compatibilizer. The blends exhibited two separate glass transitions over the entire composition range; their changes with composition indicated that PTT was partially miscible with ABS, and the miscibility of the PTT/ABS blends was improved slightly as the ABS content increased. T_m of the PTT phase in the blends was composition dependent and was depressed to lower temperatures with increasing ABS content. Both T_{cc} (PTT phase) and T_g (PTT phase) moved to higher temperatures in the presence of compatibilizers.

PTT showed crystallization exotherms at all compositions of the PTT/ABS blends, and the crystallization behavior was completely different at low and high ABS contents. At lower ABS contents (0–50 wt %), the crystallization process of the PTT phase shifted slightly to higher temperatures as the ABS content increased. At ABS ≥ 60 wt %, PTT showed fractionated crystallization. The influences of the epoxy and SBM compatibilizers on PTT's crystallization were content dependent: lower compatibilizer contents (1–3 wt % epoxy or 1 wt % SBM), retarded crystallization, and higher compatibilizer contents (5 wt %) accelerated crystallization.

The crystallization kinetics was analyzed with a modified Avrami equation. When ABS was 20–50 wt %, the temperature to reach a given relative crystallinity shifted to higher temperatures compared with that of pure PTT, but the nucleation mechanism and the growth mode remained unchanged. At 60 wt % ABS, the temperature to reach a given relative crystallinity for the bulk crystallization exotherm shifted considerably to a lower temperature, and the nucleation mechanism changed to a thermal mode.

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