Effect of a Type of Triazine on the Properties and Morphologies of Poly(butylene terephthalate) Composites

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ABSTRACT: Composites of poly(butylene terephthalate) (PBT), 2,4,6-tris(2′,4′,6′-tribromophenoxy)-1,3,5-triazine (TTA), and glass fibers were prepared, and the effect of TTA on the properties and morphologies of the composites was studied. The results showed that the addition of a suitable amount of TTA could improve the flame retardancy of PBT composites reinforced with glass fibers, and good resistance to TTA emigration from the inside of the composites onto their surfaces was obtained. Fourier transform infrared spectroscopy analyses of PBT, TTA, and their blend suggested that there might be no chemical bonds formed on the interfaces between PBT and TTA in the composite; a thermogravimetric study revealed that the weight loss of the PBT/TTA composite was very limited in the temperature range of 25–300°C, and scanning electron microscopy images of the blend demonstrated that the TTA particle sizes and their distribution in the PBT matrix remained thermally stable when the system was heated at 130°C for 3 h. This suggested good compatibility of TTA with PBT. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1291–1296, 2006

Key words: flame retardance; mechanical properties; morphology; polyesters

INTRODUCTION

The performance and processability of poly(butylene terephthalate) (PBT) as a kind of engineering plastic have been investigated extensively for the purpose of its wide use in electric appliances, electronic connectors, and car parts such as lamp holders, switches, circuit breakers, and motor casings that require PBT composites with a high flame-retardant property.[1–4] In many cases, this property of the composites can be obtained by the incorporation of flame retardants into the system. During the last several decades, flame retardants for PBT have been developed, ranging from halogen-containing flame retardants to halogen-containing polymeric flame retardants and halogen-free flame retardants.[5–11]

Despite having a number of technical advantages in applications, low-molecular-weight halogen-containing flame retardants such as decabromodiphenyl oxide (DBDPO) may be prone to emigration from the inside of the composites onto their surfaces when the composites are heated, that is, blooming on the surface of the composites due to the poor compatibility of DBDPO with the matrix, which will directly affect the properties of the composites, such as the flame-retardant and electrical properties and adhesion strength, thus resulting in difficulty in the practical use of the composites. Furthermore, the blooming of DBDPO on the surface of the products under unfavorable injection-molding conditions may cause the unwanted contamination of the surfaces of the injection mold. After some injection cycles, a layer of thick and somewhat sticky DBDPO on the mold surfaces can appear; this is called a juicing phenomenon. The use of a macromolecular flame retardant is a good way to solve the problem, but its relatively high price will certainly affect its wide range of applications. Therefore, many studies have been carried out on the possibility of the replacement of DBDPO with a kind of effective flame retardant with a low molecular weight, low price, and excellent antiblooming property.[12–15]

A kind of flame retardant with a low molecular weight, 2,4,6-tris(2′,4′,6′-tribromophenoxy)-1,3,5-triazine (TTA) has been used for the preparation of fire-resistant polyolefins and some other thermoplastic composites as well as fibers with reduced bleeding of fire retardants.[16] However, to the best of our knowledge, there has been no report on its application to PBT or PBT composites. In this article, we describe the preparation of PBT and PBT/glass-fiber composites incorporated with TTA and investigate its influence on the flame-retardant, antiblooming, and mechanical properties and morphologies of the PBT composites. Moreover, a comparison of TTA and DBDPO is made with respect to their contributions to the properties and morphologies of the composites.

EXPERIMENTAL

The PBT resin (BST L2100), provided by the Yizheng Chemical Fiber Group (People's Republic of China),

TABLE I
Recipes for PBT Sample Preparation

Sample	PBT (wt %)	Glass fiber (wt %)	TTA (wt %)	DBDPO (wt %)	Sb_2O_3 (wt %)
PBT1-1	90.0	10.0	0	0	0
PBT1-2	83.3	10.0	5.0	0	1.7
PBT1-3	76.7	10.0	10.0	0	3.3
PBT1-4	70.0	10.0	15.0	0	5.0
PBT2-1	100.0	0	0	0	0
PBT2-2	93.3	0	5.0	0	1.7
PBT2-3	86.7	0	10.0	0	3.3
PBT2-4	80.0	0	15.0	0	5.0
PBT3-1	86.7	0	0	10.0	3.3
PBT3-2	76.7	10.0	0	10.0	3.3
PBT3-3	66.7	20.0	0	10.0	3.3
PBT3-4	56.7	30.0	0	10.0	3.3

was in the form of pellets with an intrinsic viscosity of 1.00 dL/g, a carboxyl end group concentration of 30 mmol/kg or less, a melting point of 225°C or higher, a color L value of 90 or higher, a color b value of 3.5 or less, a specific gravity of 1.30–1.32 g/cm^3, a melt flow index of 23–28 g/10 min, a tensile strength of 50–60 MPa, an elongation value of 200% or higher, a notched Izod impact strength of 40 J/m or higher, and a dielectric strength of 20 kV/mm or higher. TTA, a white powder with a specific gravity of 2.44 g/cm^3, a purity grade of 95%, and a theoretical bromine concentration of 66.7 wt %, was supplied by the Nanjing Research and Design Institute of Chemical Industry. DBDPO (DE-83R) was acquired from Great Lake (United States). The short, cut E-glass fiber was in the form of chopped strands with a diameter of 13 μm and a length of 3 mm (183 Fiberglass, Owens–Coring Fiberglass Corp.).

The recipes for the sample preparation are listed in Table I; the total amount of a sample was 100 parts in weight, and the ratio of TTA or DBDPO to Sb_2O_3 was 3:1 because of the practical use of a recipe in industry and the synergistic flame-retardant effect. A typical sample preparation process was as follows. A mixture of thoroughly dried materials (PBT, flame retardants, and glass fibers) was melt-blended in a contrarotating, twin-screw extruder (TE-35, Keya Plastic Machine Factory) with a diameter of 36 mm and a ratio of the length to the diameter of 36. The blend was then granulated. The screw speed of the extruder was 160 rpm, and the temperatures of the four bands of the barrel from the feed section to the die of the extruder were 245, 250, 250, 255, and 250°C, respectively. The samples for testing the mechanical properties were prepared by injection molding. The temperatures of the three zones in the injection-molding machine (CJ80M3V, Zhengde Plastic Machine Factory) were 235, 240, and 240°C. The mold temperature was about 80°C, and the injection pressure was maintained at 50 MPa. The times for the injection, cooling, and ejection

stages were 40, 20, and 1 s, respectively. The pellets were melted and injected into a family mold that consisted of bars for tensile testing (ASTM D 638), Izod impact testing (ASTM D 256), and flexural testing (ASTM D 790A). The bars for the Izod impact test were then notched according to ASTM D 256.

The tensile strength, flexural strength, and notched Izod impact strength of the samples were measured according to related ASTM standards at 23°C. Ten specimens were tested, and their results were averaged for every datum. The notched Izod impact strength test was carried out with a UJ-4 impact tester (Chengde Test Equipment Co., Ltd.); the tensile strength and flexural strength measurements were made on a CMT5254 tensile tester (Precision Rank 0.5, Xin San Si Measurement Technology Co., Ltd.). Limiting oxygen index (LOI) tests of the samples were conducted with an HC-2 oxygen index instrument (Jiangning Analysis Instrument Factory) according to ASTM D 2863; the specimen size was 0.65 cm $\times$ 0.3 cm $\times$ 7–15 cm. The melt flow index of the samples was obtained at 230°C with a load of 2.16 kg (ASTM D 1238) with an XNR-400A melt flow indexer (Changchun Second Test Machine Factory). We evaluated the blooming performance of the flame retardants on the surface of the PBT composites by rubbing them against the surface of the samples, which were heated in air at 130°C for 3 h, and then observing whether or not an off-white powder appeared.

The structures of flame retardant TTA, PBT, and PBT composites were analyzed with the help of their Fourier transform infrared (FTIR) spectra, which were recorded from either a KBr/TTA powder mixture or films of PBT and its composites with an FTIR spectrophotometer (Nexus 670 FTIR, Nicolet Co., United States). The number of scans per spectrum was 24, and the spectral resolution was 2 cm^{-1}. Before the FTIR measurements, the samples were dried *in vacuo* overnight. The films of PBT and its composites were prepared via hot pressing at 220°C. The sample morphology was observed with scanning electron microscopy (SEM; JSM-5900, JEOLTD/Japan Electric) at an accelerating voltage of 15 kV and a probe current of 20 pA. For SEM measurements, the injection-molded bars were freeze-fractured at the temperature of liquid N_2 and then sputter-coated with gold with an JFC-1600 auto fine coater. Thermogravimetric analysis (TGA) of TTA, its composite with PBT, and DBDPO was carried out with a Netzsch analyzer between 25 and 300°C in air at a heating rate of 5°C/min. All samples were dried *in vacuo* at room temperature for 24 h before the TGA runs.

RESULTS AND DISCUSSION

Flame-retardant properties are very important for PBT and its glass-fiber-reinforced composites in many

TABLE II
Comparison of the Blooming Performances of TTA and DBDPO from PBT Composites

Sample	PBT1-3	PBT1-4	PBT2-3	PBT2-4	PBT3-1	PBT3-2	PBT3-3	PBT3-4
Blooming	●	●	●	●	○	○	○	○

○ = blooming; ● = nonblooming.

cases. However, if the flame retardant incorporated into the PBT system is not compatible with the matrix and continues to transfer to the surfaces of the products in use, the flame-retardant properties of the products will be severely degraded after use for some period of time. Therefore, nonblooming characteristics of the flame retardant are required to maintain the permanent flame-retardant properties of the products under their use conditions. In this respect, the blooming performance of TTA from PBT composites and a comparison of this behavior of TTA with that of DB-DPO commonly used in industry were investigated; the results are summarized in Table II. When flame retardants TTA and DBDPO were added to PBT composites, their blooming performances were strikingly different. For the PBT blends with flame retardant TTA, no frost phenomenon could be observed on their surfaces even after the composite containing as much as 15 wt % TTA was heated at 130°C for 3 h. The results indicated that no observable number of TTA particles could emigrate onto the surface from the inside of the composite, probably because of the good compatibility of TTA with the matrix; therefore, TTA demonstrated an excellent antiblooming ability. However, off-white frost could be easily and quickly found on the surface of PBT containing 10 wt % DBDPO when the blend was heated for a very short time at the same temperature at which the PBT/TTA composite was heated. Further experiments showed that DBDPO blooming could occur even if a very low amount of the flame retardant was added to the PBT system, suggesting that thermal emigration of the flame retardant from the inside of the composite onto its surface could easily take place because of the incompatibility of DBDPO with the polymer matrix.

The effects of different amounts of PBT and TTA together with Sb_2O_3 on the mechanical and flame-retardant properties of PBT and its composites reinforced with glass fibers are demonstrated in Table III (entries 1–8). The tensile strength remained stable for either PBT/TTA or PBT/TTA/glass-fiber composites, regardless of the amounts of the components in the range of our study. The addition of TTA and the synergistic flame retardant Sb_2O_3 initially made the flexural strength of the composites in both cases slightly better, but the improvement leveled off when the concentration of TTA was larger than about 5 wt %. The tensile and flexural properties of the composites suggested favorable interactions between TTA

and PBT because an ordinary filler normally has a negative effect on the mechanical properties of its composites with polymers. Moreover, the PBT composite reinforced with 10 wt % glass fiber showed tensile and flexural strengths of about 80 and 110 MPa, respectively, exhibiting much better mechanical properties than the PBT/TTA composite to which no glass fiber was added. These results could be easily understood with respect to the contribution by the glass fiber. However, the notched Izod impact strength of the composites either with or without glass-fiber reinforcement deteriorated with increasing amounts of TTA and Sb_2O_3; moreover, a higher impact strength was obtained when glass fiber was added to the PBT/TTA composite. This was similar to the case of the tensile and flexural strengths. Generally, the impact strength of materials is related to the bond strength of molecules and polymer chain movement under certain stress, as well as the stress distributions in the materials caused by this movement. In other words, the impact strength actually reflects the flexibility of the materials. For glass-fiber-reinforced PBT composites, the good flexibility of the PBT chain makes the energy transmission easier on the one hand; on the other hand, the interface of the glass fiber and matrix is improved after the glass-fiber surface treatment. Under these conditions, the impact load can be easily transmitted from the matrix to the glass fiber, leading to the so-called crazing phenomenon in the composite.

TABLE III
Mechanical and Flame-Retardant Properties of PBT Composites Reinforced with Different Contents of Glass Fibers

Sample	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/m)	Flame retardancy LOI (%)
PBT1-1	77.6	107.7	57.1	20.2
PBT1-2	80.3	114.0	54.3	21.0
PBT1-3	80.0	115.5	48.4	25.6
PBT1-4	83.3	115.7	38.2	31.3
PBT2-1	57.1	83.2	47.4	23.3
PBT2-2	59.1	98.7	44.3	23.5
PBT2-3	57.8	100.0	36.4	23.5
PBT2-4	60.5	100.0	32.3	24.7
PBT3-1	56.5	107.0	33.0	24.1
PBT3-2	64.1	115.8	43.4	25.2
PBT3-3	89.1	134.7	64.9	32.8
PBT3-4	109.3	155.6	81.2	33.5

In this way, the impact strength of PBT composites would be improved by the addition of glass fiber. Moreover, the effect of glass fiber on the fluidity of PBT/TTA composite was investigated. The melt flow index of PBT containing 10.0 wt % TTA and 3.3 wt % Sb_2O_3 exhibited a trend of a steady decline with an increasing amount of glass fiber, indicating that the addition of glass fiber reduced the fluidity of the composite because it enhanced the inner friction in the composite, therefore hindering the flow of the melting composite.

For comparison, measurements of the mechanical properties of PBT/DBDPO composites with and without glass-fiber reinforcement were carried out, and the results are summarized in Table III. The data listed in entries 3 and 10 and entries 7 and 9 of Table III indicate that both PBT and its composite with 10 wt % glass fiber, when incorporated with TTA, had properties similar to those when they were incorporated with DBDPO, with the exception of the tensile strengths of the glass-fiber-reinforced composites.

According to Table III (column 5), the LOI, that is, the flame retardancy of the composites, strengthened with the amount of TTA, and this trend was even obvious when the amount of TTA increased from 5 to 15 wt % for the glass-fiber-reinforced PBT composite; however, only a slight increase in the flame retardancy could be attained for the composite without glass fiber. Very interestingly, when the addition of TTA was less than around 8 wt %, the PBT/TTA/glass-fiber composite did not show as good a flame-retardant property as the PBT/TTA composite; however, this property of the former composite was improved greatly when the amount of TTA exceeded the critical point. There is no doubt that the difference in the flame retardancy for the two composites should be attributed to the glass-fiber contribution. It is believed that glass fiber self-behaves as a flame retardant; at the same time, its interface with the matrix may provide more opportunities for flame. Therefore, the total effect of glass fiber on the flame retardancy of a composite should be dependant on which factor is dominant in the system. Similar results for DBDPO/PBT and its glass-fiber composite (Table III) could offer strong support for this explanation. Thus, it can be concluded that both the mechanical properties and flame retardancy of PBT composites will be affected by the addition of TTA and glass fiber, and the amounts of the addition should be optimized with respect to the comprehensive properties of the composites.

The thermal resistance of TTA, the PBT/TTA/Sb_2O_3 (80/15/5 w/w/w) composite, and DBDPO is demonstrated in Figure 1. The weight losses of TTA, its composite with PBT, and DBDPO were 1.4, 2.7, and 1.7%, respectively, quite similar if the errors of the measurements were considered. Obviously, the fire
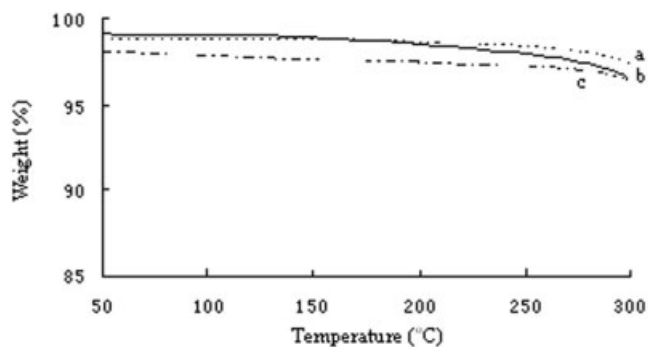
Figure 1 TGA curves for (a) TTA, (b) the PBT/TTA/Sb_2O_3 (80/15/5 w/w/w) composite, and (c) DBDPO.

retardants and PBT composite remained thermally stable in the temperature range of our study; therefore, HBr evolved and the corrosion caused in this time was very limited.

The properties of PBT composites certainly depend on the components of the composites and the structures and interfacial actions of the components; therefore, FTIR and SEM investigations of PBT composites were carried out. The FTIR spectra of pure PBT, flame retardant TTA, and their composite are given in Figure 2. In the case of pure PBT, a strong characteristic band at 1713 cm^{-1} was due to the absorption of the carbonyl group, and the absorption peaks in the 1457–1577-cm^{-1} region could be assigned to the stretching vibration of the benzene ring and C—H bending of methylene. The broad and strong absorption band near 2962 cm^{-1} could be used to characterize the C—H stretching vibration of the benzene ring and —CH$_2$— in the PBT skeleton. Moreover, the absorption peaks in the 680–1000-cm^{-1} region from out-of-plane C—H bending of the benzene ring could be observed. For the FTIR spectrum of TTA, strong bands at 1234 cm^{-1} and in the 1360–1583-cm^{-1} region corresponded to the C—O—C vibration of aromatic ether and stretching motions of both benzene and triazine rings, respectively. The weak peak at 620 cm^{-1} was attributed to the characteristic absorption of C—Br. The FTIR spectrum of the PBT/TTA composite shows that the addition of TTA neither changed the characteristic bands of pure PBT nor produced new absorption bands, suggesting that there might be no new chemical bonds formed between TTA and PBT in the composite. However, the flame retardant indeed had an excellent antiblooming ability, as discussed previously; therefore, the good compatibility of TTA with PBT, which could lead to a stable dispersion of TTA in the matrix, may make it understandable why no observable thermal emigration of TTA from the inside of the matrix onto its surface could occur.

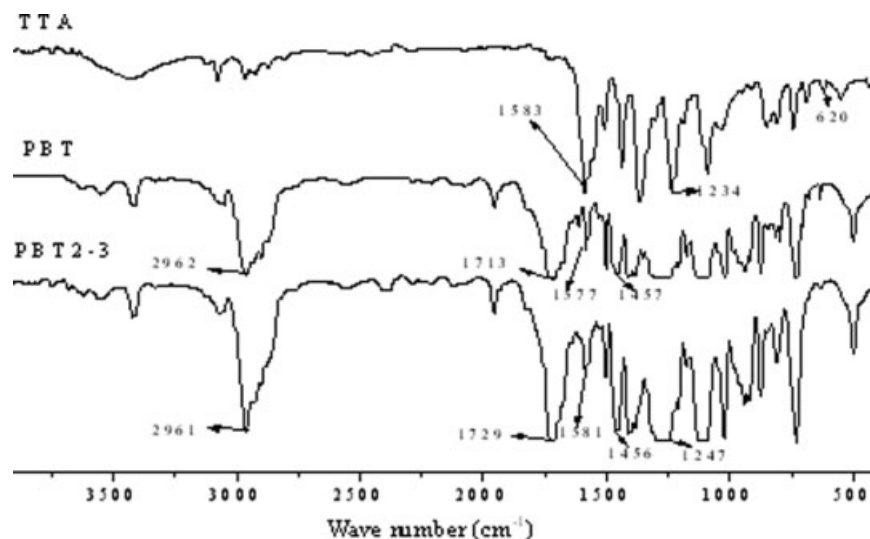The morphology of the PBT composites with both TTA and DBDPO was investigated with SEM. Figure

Figure 2 FTIR spectra of TTA, PBT, and their composite.

3 shows the results of fractured surfaces of the PBT/TTA (90/10 w/w) composite with different thermal histories. As shown in Figure 3(a), TTA particles were well dispersed in the PBT matrix before heating. Moreover, the dispersion of TTA particles remained

Figure 3 SEM micrographs of PBT/TTA composites (90/10 w/w): (a) before heating and (b) after heating at 130°C for 3 h.

stable even after the sample was heated at 130°C for 3 h [Fig. 3(b)]. A close inspection of the SEM images with relatively high magnification for the same samples indicated that the particle sizes, their distribution, and the dispersion of the fire retardant remained stable when the composite was under different thermal conditions; this provides convincing evident for the good compatibility of TTA and PBT. The combination of these SEM results and the FTIR spectra should give a reasonable explanation for the excellent antiblooming property of TTA in the PBT composites because no obviously observable amount of TTA emigrated from the inside of the composite onto its surface according to the thermally stable sizes, size distribution, and dispersion of TTA particles in the PBT composite.

The SEM micrographs of fractured surfaces of the PBT/DBDPO (90/10 w/w) blend under different thermal environments are illustrated in Figure 4(a,b). Small DBDPO particles were relatively well dispersed in the PBT matrix before heating [Fig. 4(a)]. However, when the composite was heated for a short time, the DBDPO particles were prone to agglomerate in the inside of the blend; therefore, many large DBDPO particles were detected [Fig. 4(b)]. Moreover, a poor TTA distribution and obvious changes in the particle size distribution in the composite were observed because of the agglomeration of DBDPO particles and their thermal emigration from the inside of the composite onto its surface to reduce the surface energy of the particles and increase their stability in the PBT matrix. Therefore, the phenomenon of whitening appearing on the surface of the composite inevitably occurred, and this was in good agreement with our observations. These results suggested that the compatibility of DBDPO with PBT should not be as good as that of TTA with PBT.
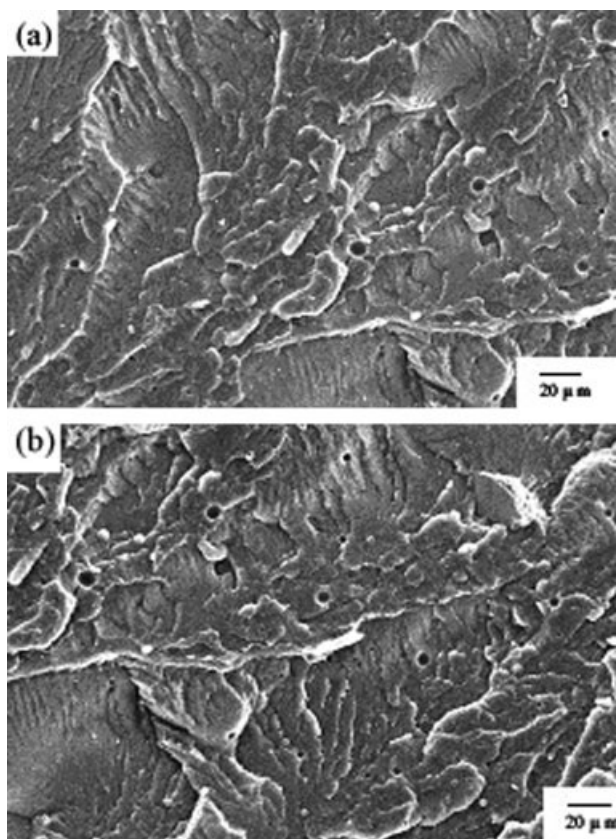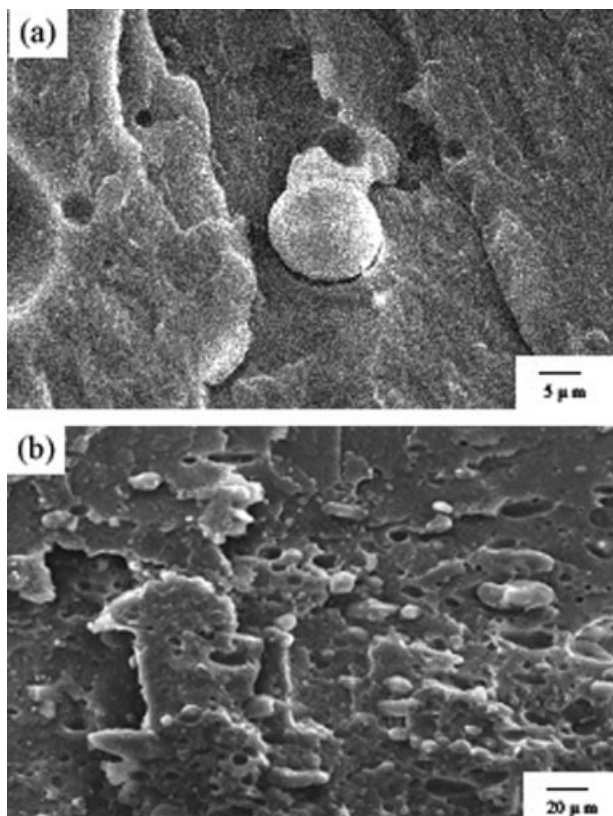
Figure 4 SEM micrographs of PBT/DBDPO composites (90/10 w/w): (a) before heating and (b) after heating at 130°C for 10 min.

The reasons for the great difference in the compatibilities of TTA and DBDPO with PBT are not known. The following factors can be considered. Obviously, TTA and DBDPO are different in terms of components and structure, and the molecular weight and spherical hindrance of TTA are definitely larger than those of DBDPO. Moreover, it seems that DBDPO particles in the PBT matrix are spherical and cylinder-like before and after agglomeration, respectively, with a relatively smooth surface morphology. The interfaces between the DBDPO particles and PBT matrix is clear. However, compared with DBDPO, TTA particles are smaller, more irregular, and nearly monodisperse; their surfaces appear to be somewhat uneven.

CONCLUSIONS

A type of triazine (TTA), when incorporated into PBT/glass-fiber composites as a flame retardant, can obviously improve the flame retardancy of the composites and keep good resistance to its emigration from the inside of the composites onto their surface when the composites are heated. The excellent anti-blooming property of TTA can be attributed to its good compatibility with the PBT matrix because the structure analysis by FTIR suggests that there are no chemical bonds formed on the interfaces of the TTA particles and PBT matrix in the PBT/TTA blend, and morphology images by SEM indicate that the particle sizes and their distribution in the matrix remain thermally stable. The tensile and flexural strengths of PBT composites remain stable, but the impact strength deteriorates with an increasing amount of TTA. In contrast, DBDPO exhibits a great capacity for blooming on the surface of PBT composites. SEM studies reveal that DBDPO particles are prone to aggregate in DBDPO/PBT blends, which are supposed to be heated for a short time, suggesting that the compatibility of DBDPO is not as good as that of TTA with PBT.

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