Investigations of Thermal Degradation Behavior and Fire Performance of Halogen-Free Flame Retardant Poly(1,4-butylene terephthalate) Composites

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ABSTRACT: This work aims to develop halogen-free poly(1,4-butylene terephthalate) (PBT) composites with enhanced flame retardancy using ecofriendly flame retardants, aluminum hypophosphite (AHP) and melamine derivatives (melamine polyphosphate and melamine cyanurate). Microscale combustion calorimetry and thermal gravimetric analysis/infrared spectrometry (TG-IR) technique were used to investigate the potential fire hazards of these PBT composites. For the PBT composites with the incorporation of AHP and melamine derivatives, the heat release capacity (HRC) which is an indicator of a material fire hazard was significantly reduced, and the intensities of a variety of combustible or toxic gases detected by TG-IR technique were remarkably decreased. Moreover, a loading of 20 wt % flame retardant mixture fulfilled the PBT composites high limited oxygen index (LOI) and V-0 classification in UL 94 testing. An intumescent flame retarded mechanism was speculated in this work, because numerous bubble-like char residues were found on the surface of the samples containing flame retardant mixture after LOI testing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1480–1488, 2011

Key words: polyesters; polymer blends; thermogravimetric analysis (TGA); flame retardance; intumescence

INTRODUCTION

Represented by poly(ethylene terephthalate) (PET) and poly(1,4-butylene terephthalate) (PBT), partly aromatic polyesters are commonly used as engineering plastics in electrical and electronic industries. Because of the good dimensional stability and thermal resistance, PBT was introduced in 1970 and its utilization grew rapidly in high volume automotive, electrical, and other engineering applications.[1,2] However, the development and application of PBT were limited due to its flammability and serious dripping when subjected to elevated temperature or combustion. In addition, there would be amounts of toxic gases, soot, and smoke, which are a health and environmental impediment to the full implementation of PBT in numerous engineering designs during the combustion or thermal degradation process. Consequently, it is necessary for academic institutions and industrial laboratories to fabricate fire retarded PBT composites.

The flame-retardant systems which have been most commonly used for polyesters consist of halogenated additives, but the application of halogen-containing additives has been forbidden in many countries due to the release of toxic and corrosive gases. Therefore, the development of halogen-free flame retarded polyesters is strongly demanded. In the past decades, phosphorus-based intumescent systems were frequently used to manufacture flame retardant polyester composites. In our previous study,[3] the fire retardant efficiency of melamine (MA) and triphenyl phosphate (TPP) in PBT was studied by the limiting oxygen index (LOI) and the UL 94 test. On adding 10 wt % MA and 20 wt %
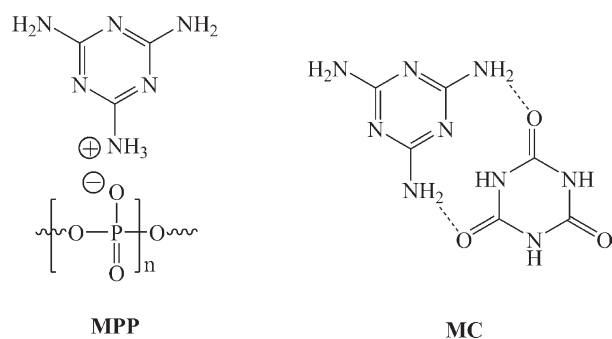
Figure 1 Chemical structures of MPP and MC.

TPP, LOI increased from 20.9 to 26.6 and the UL 94 V-0 rating was achieved. Balabanovich et al.[4] prepared self-extinguishing PBT composites (V-0 rating) by the addition of 15 wt % ammonium polyphosphate (APP) and 10 wt % 2-methyl-1,2-oxaphospholan-5-one 2-oxide (OP). They considered that the fire retarded effect was attributed to the condensed-phase mechanism of intumescence. In fact, most intumescent flame retardants are not suitable for the preparation of fire retarded PBT composites, because of the high processing temperature and sensitivity to degradation caused by reactive chemical species. Moreover, high loadings of flame retardants could cause harmful effects to the mechanical properties of polymer matrix.

Metal salts of alkylphosphinic acid have been found to be particularly effective in polyesters.[5–9] Braun et al.[5] investigated the flame retardancy mechanisms of aluminum diethylphosphinate and its combination with melamine cyanurate in glass-fiber reinforced poly(butylene terephthalate) composites. Both the gas-phase and solid-phase actions caused by aluminum diethylphosphinate were revealed in this work. Meanwhile, a UL 94, V-0 rating composite material was achieved at a loading of 20 wt %. In their subsequent study,[6] aluminum diethylphosphinate was used to fabricate flame retarded PBT composites. The addition of 10 wt % aluminum diethylphosphinate to PBT improved flame retardancy in the cone calorimeter and UL 94 testing, thanks to the predominant gas-phase effect and condensed-phase action. Although these organic phosphinate salts have been proved to be greatly efficient for PBT, the manufacture of these salts on an industrial scale is relatively complex and expensive, thereby limiting the possibilities of using the products as flame retardants.[9]

The present study chooses commercial flame retardants, aluminum hypophosphite (AHP) and melamine derivatives, to develop environmentally friendly fire retarded PBT composites with enhanced flame retardancy. The chemical formula of AHP is $Al(H_2PO_2)_3$ which can be easily synthesized on an industrial scale. The use of melamine derivatives as a synergist for phosphorous flame retardants in polyester has been established.[3,5,10] Therefore, melamine polyphosphate (MPP) and melamine cyanurate (MC) are used as synergists in this work. The aim of this research is to combine the fire retarded potential of AHP and melamine derivatives to significantly improve the flame retardancy of PBT composites. The formulations in this work will be investigated for the contributions to possible fire hazards using microscale combustion calorimetry and thermal gravimetric analysis/infrared spectrometry technique. Furthermore, the thermal degradation behavior and fire performance of these formulations will be studied, and the flame retardancy mechanism of optimized formulations will be established.

EXPERIMENTAL

Materials and preparation

In this work, poly(1,4-butylene terephthalate) (PBT) (4500) was a product of BASF Chemical Company, Germany. Melamine polyphosphate (MPP) was provided by Shandong Shian Chemical Co., Ltd, China. Melamine cyanurate (MC) was a commercial product from Shandong Shouguang Weidong Chemical Engineering Co., Ltd, China. The chemical structure of MPP and MC were shown in Figure 1. Aluminum hypophosphite (AHP) was supplied by Qingzhou Yichao Chemical Co., Ltd, China.

PBT and all additives were dried at 80°C overnight before use. PBT was blended with additives using a twin-roll mill (XK-160, made in Jiangsu, China) at 235°C for 10 min. The roller speed was 100 rpm for the preparation of all the samples. They were then molded by using a hot press at 235°C to obtain 3.2 mm thick plaques. Compositions and designations of the studied composites are listed in Table I.

Thermal degradation analysis

Thermogravimetric analysis (TGA) was carried out using a Q5000 IR thermogravimetric analyzer (TA Instruments Waters, China) at a linear heating rate

TABLE I
Examined Formulations

| Sample | Composition (wt %) | | | |
	PBT	AHP	MPP	MC
PBT	100	0	0	0
PBT/MPP5	95	0	5	0
PBT/MC5	95	0	0	5
PBT/AHP15	85	15	0	0
PBT/AHP10/MPP5	85	10	5	0
PBT/Al10/MC5	85	10	0	5
PBT/AHP20	80	20	0	0
PBT/AHP15/MPP5	80	15	5	0
PBT/AHP15/MC5	80	15	0	5
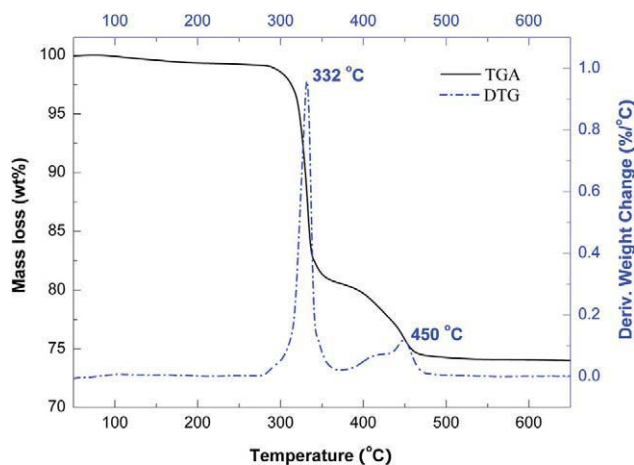
Figure 2 TGA and DTG curves of AHP in a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 20°C/min under nitrogen condition. The weight of all the samples were kept within 5 to 10 mg. Composites in an open Pt pan were tested under an airflow rate of 6×10^{-5} m^3 per minute at temperature ranging from room temperature to 700°C.

Thermogravimetric analysis/infrared spectrometry (TG-IR) of PBT composites had been performed using the TGA Q5000 IR thermogravimetric analyzer interfaced to the Nicolet 6700 FTIR spectrophotometer. About 5.0 mg of each composite was put in an alumina crucible and heated from 30 to 700°C. The heating rate was set as 20°C/min in a nitrogen atmosphere with a flow rate of 45 mL/min.

Thermal combustion properties

Thermal combustion properties of PBT composites were measured using a microscale combustion calorimetry (MCC, Govmark) according to ASTM D 7309-07. Four to 8 mg of each sample was weighed with a microbalance and placed in a Pyroprobe (CDS Analytical Model 2000) for rapid pyrolysis in a pyrolysis-combustion flow calorimeter. A special probe was placed into a heated interface continuously purged with pure nitrogen. Then programming the system to heat at 1°C/s from 90 to 600°C and held there for 30 s. During pyrolysis, the volatilized decomposition products are transferred in the stream of nitrogen to a high-temperature combustion furnace where pure oxygen is added and the decomposition products are completely combusted. The amount of oxygen consumed is measured with an oxygen analyzer and used to calculate a heat release rate (HRR). All MCC data obtained were reproducible to about ±3%.

Flammability testing

The flammability properties of studied formulations were determined by limited oxygen index (LOI) and

Underwriters Laboratories (UL) 94 test according to ASTM D2863 and ASTM D3801 respectively. An HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) was used in the LOI test. The specimens used for the test were of dimensions $100 \times 6.5 \times 3$ mm^3. UL-94 test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China). The specimens used were of dimensions $130 \times 13 \times 3$ mm^3.

Residue analysis

Fourier transform infrared spectra spectroscopy (Nicolet 6700 FT-IR spectrophotometer) was employed to characterize the residues collected in LOI tests using thin KBr disc. The transition mode was used and the wavenumber range was set from 4000 to 500 cm^{-1}.

The residues collected after LOI tests were further analyzed by the scanning electron microscope (SEM). The SEM micrographs of the PBT composites were obtained with a scanning electron microscope AMRAY1000B at an accelerating voltage of 20 kV. The specimens were sputter-coated with a conductive layer.

RESULTS AND DISCUSSION

Thermal degradation behavior

The thermal decomposition of AHP is characterized by two steps with two maximal mass loss rates at 332°C and 450°C (Fig. 2). The decomposition process of AHP could be represented by the two equations as detailed below:

$$2Al(H_2PO_2)_3 \xrightarrow{\Delta} Al_2(HPO_4)_3 + 3PH_3$$

$$2Al_2(HPO_4)_3 \xrightarrow{\Delta} Al_4(P_2O_7)_3 + 3H_2O$$
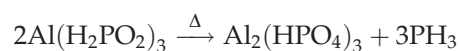
PH$_3$ and H$_2$O are the main decomposition products of AHP at the first and second step respectively, leaving the residue Al$_4$(P$_2$O$_7$)$_3$ of 74 wt %.

The TGA results of neat PBT and PBT composites are summarized in Table II and shown in Figure 3, respectively. The thermal degradation curve of neat PBT in a nitrogen atmosphere is characterized by a single decomposition step beginning from 362°C (T$_{-3\%}$). The resulting residue is only of about 2.9 wt %. When MPP is added, the degradation behavior has no fundamental change. The initial decomposition of PBT/MPP5 is shifted to a temperature of about 7°C lower. At the end of the test, the residue slightly increases to 3.9 wt %. The initial decomposition temperature of PBT/MC begins from 347°C. In comparison with MPP, the addition of MC reduces the thermal stability of PBT composite more seriously.

TABLE II
TGA Data Under Nitrogen Condition for Neat PBT and
Its Composites

| Sample	$T_{-3\%}$ (°C)	$T_{-50\%}$ (°C)	Residue (wt %) at 700°C
PBT	362	399	2.9
PBT/MPP5	355	397	3.9
PBT/MC5	347	399	3.2
PBT/AHP15	342	395	19.0
PBT/AHP10/MPP5	340	393	14.8
PBT/AHP10/MC5	331	395	14.2
PBT/AHP20	335	395	24.1
PBT/AHP15/MPP5	333	393	19.0
PBT/AHP15/MC5	331	395	18.7

The addition of AHP to PBT also influences the degradation process. The first decomposition step of PBT/AHP15 is shifted to decomposition temperature about 20°C lower, which is caused by the pyrolysis of AHP. The thermally stable residue at 700°C is significantly increased to 19 wt %. It has been known that the mass loss is about 26 wt % in the thermal decomposition process of AHP from room temperature to 700°C. Therefore, the high content of residue after the degradation of PBT/AHP15 demonstrates that the presence of AHP remarkably promotes the char forming. When the melamine derivatives and AHP are combined in PBT, the degradation process is similar with that of PBT/AHP15. The further reduction of decomposition temperature is attributed to the pyrolysis of the additives. When the fraction of AHP increases, the thermal stability of PBT composites is further reduced. However, the decomposition temperatures of PBT composites at mass loss of 50 wt % were not drastically influenced by the introduction of flame retardant additives.

The results of TG indicate a strong interaction between the additives and the polymer matrix. The interaction between flame retardants and PBT induces a shift in decomposition temperature. When melamine derivatives and AHP are combined, the further reduction of decomposition temperature occurs. In fact, most of the flame retardants containing phosphorus or nitrogen would decrease the thermal stability of neat polymers, because either condensed-phase or gas-phase dilution action needs to be effective before the drastic degradation of polymer matrix. In the current work, the addition of flame retardants mildly reduces the initial decomposition temperature of PBT matrix. On the other hand, the strong interaction between AHP and the polymer leads to the formation of amounts of residues which may cover on the surface of polymer matrix to inhibit the release of volatilization products.

Degradation products

Identification of degradation products was studied by the TG-IR technique, which can help to under-

stand the thermal degradation mechanism for polymers. In this work, the optimized formulations (PBT/AHP20, PBT/AHP15/MPP5, and PBT/AHP15/MC5) were investigated by means of TG-IR technique. Because the gas phase products from the decomposition of PBT/AHP20 and PBT/AHP15/MC5 are similar with that of PBT/AHP15/MPP5, the 3D TG-IR spectrum of volatiles for the thermal degradation of PBT/AHP15/MPP5 is only studied in detail, which is shown in Figure 4. An additional peak occurs at the sixteenth minute in the thermal degradation process, which is attributed to the initial decomposition stage of AHP and MPP beginning from about 310°C. The wide absorption peak above 3500 cm^{-1} is detected during the maximum mass loss rate, which should correspond to the release of H_2O caused by the degradation of AHP or the interaction between AHP and PBT. To study the change of these volatilized products more clearly, major signals from the gas phase spectrum changing with time are separated from the three-dimensional spectra shown in Figure 5. The main signals are assigned and summarized in Table III.
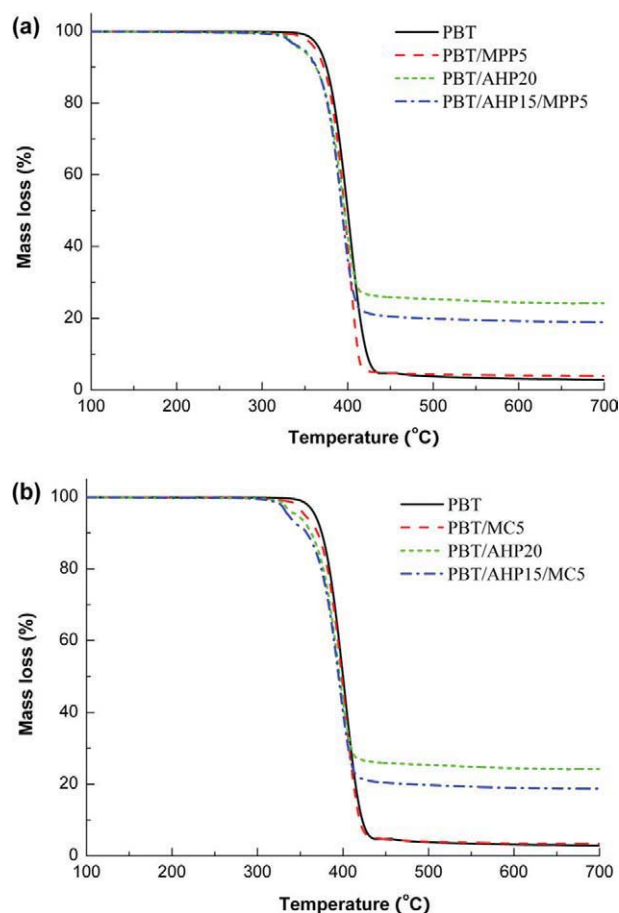

Figure 3 TGA curves of the investigated composites in a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
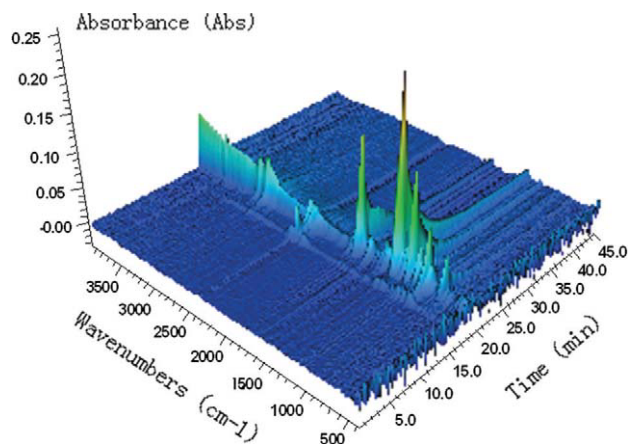
Figure 4 Three-dimensional surface graph for the FTIR spectra of the evolved gases produced by PBT/AHP15/MPP5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The main evolved gases from thermal degradation of PBT include butadiene, carbon dioxide, tetrahydrofuran (THF), benzene, and ester derivatives. From the detected gas products during thermal degradation of PBT/AHP/MPP as shown in Figure 5, it can be observed that phosphine (PH_3, 2319 and 988 cm^{-1})[11] occurs at 337°C, which is the gas phase product in the initial decomposition stage of AHP. CO_2 (2356 cm^{-1}) is detected during the initial decomposition step at 367°C, and the signal becomes weak from 397°C. During the maximum mass loss rate (397°C), butadiene (908 cm^{-1}), CO_2 (2356 and 668 cm^{-1}), THF (2962 and 1023 cm^{-1}), benzene (3102, 1593, and 735 cm^{-1}), and esters (1724, 1267, and 1105 cm^{-1}) are all released. A peak at 3584 cm^{-1} should be attributed to H_2O. Subsequently, major signals for the gas phase become weak. In
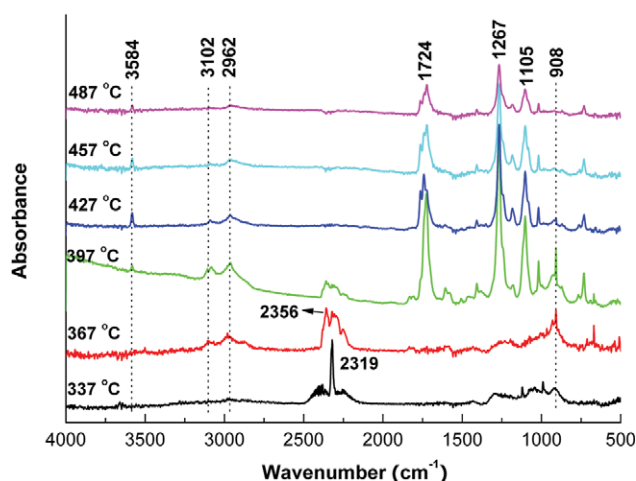
Figure 5 FTIR spectra of volatilized products at various temperatures during the thermal decomposition of PBT/AHP15/MPP5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
**Characteristic Attribution of FTIR Absorption Bands**

Band position (cm^{-1})	Assignment
908	Butadiene
1724, 1267, 1105	Esters
2962, 1023	Tetrahydrofuran
2356, 669	CO_2
2319, 988	PH_3
3102, 1593, 735	Benzene
3584	H_2O

general, PBT decomposes mainly through an intramolecular six-member cyclic transaction state, resulting in the release of terephthalic acid and butadiene.[2] The fact that the release of esters at 367°C is significantly reduced demonstrates that the condensed phase product in the first decomposition stage of AHP, $Al_2(HPO_4)_3$, probably reacts with aromatic products from the PBT decomposition. In the subsequent decomposition stage, esters and plenty of water are detected. The results indicate that the presence of flame retardants does not fundamentally change the evolved products in the gas phase, but potentially influences the product release rate.

To further understand the relationship between the additives and the product release rate, the absorbance of pyrolysis products for PBT/AHP20, PBT/AHP15/MPP5, and PBT/AHP15/MC5 versus temperature is revealed in Figure 6. Figure 6(a) illustrates the absorbance intensity of the total gases (Gram-Schmidt) for the three composites. The other three figures show the absorbance intensity of THF, esters, and butadiene, respectively. It is seen that the presence of MPP or MC in PBT/AHP composite reduces the total released volatiles in comparison with that of PBT/AHP. From Figure 6(b,c), it is observed that the release of THF and esters for PBT/AHP15/MPP5 and PBT/AHP15/MC5 respectively, are significantly retarded. Furthermore, the content of the released volatiles for PBT/AHP15/MC5 is lower than that of PBT/AHP15/MPP5. These results show that the addition of melamine derivatives can further inhibit the release of toxic or combustible products leading to the reduction of fire hazards in the PBT composites during the degradation or combustion process.

Thermal combustion properties

Thermal combustion properties were characterized by microscale combustion calorimetry (MCC) that directly measures the heat of combustion of the gases evolved during controlled heating of milligram-sized samples, which separately reproduces the gas and condensed phase processes of flaming combustion in a nonflaming laboratory test and forces them to completion to obtain intrinsic/material combustion
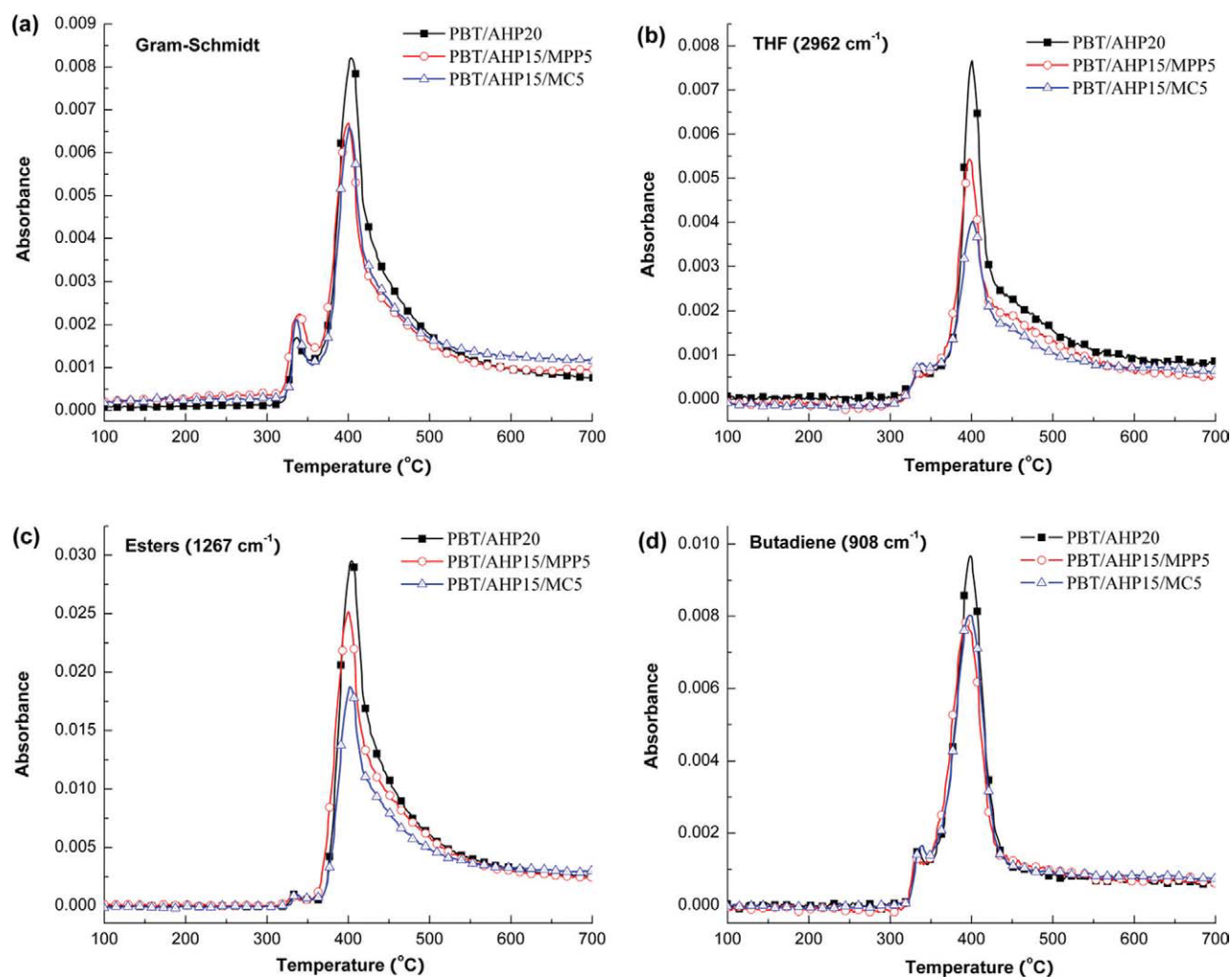
Figure 6 Absorbance of pyrolysis products for PBT/AHP20, PBT/AHP15/MPP5 and PBT/AHP15/MC5 versus temperature: (a) Gram-Schmidt; (b) THF; (c) Esters; (d) Butadiene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

properties.[12] In the present work, all formulations were screened by MCC test. All of the heat release data and the optimized heat release rate curves are summarized in Table IV and shown in Figure 7, respectively. Pure PBT is a flammable polymeric material which has high peak of heat release rate (PHRR), heat release capacity (HRC) and total heat release (THR) (Table IV). When adding 5 wt % MPP to PBT, the PHRR of PBT/MPP5 increases. The reason may be that phosphorus-based additives can induce the decomposition of PBT matrix, but there is no barrier effect caused by condensed phase to inhibit the release of combustible gases. However, the THR for PBT/MPP5 is reduced. The addition of MC or AHP slightly decreases the PHRR and THR of PBT composites. In combination with the thermal degradation analysis, the decreased THR for PBT/AHP15 is mainly caused by the condensed-phase action. The THRs of PBT/MPP5 and PBT/MC5 decrease resulting of the gas-phase dilution effect. On the other hand, the temperatures at PHRR (T_{PHRR}) of PBT/

MPP5 and PBT/MC5 are higher than that of pure PBT, because numerous inert gases from the decomposition of melamine derivatives dilute the concentration combustible gases leading to the increase of

TABLE IV
MCC Results for the Neat PBT and Its Composites

Sample	HRC (J/g·K)	PHRR (W/g)	THR (kJ/g)	T_{PHRR} (°C)
PBT	486	485	18.7	412
PBT/MPP5	673	674	17.4	420
PBT/MC5	469	459	18.5	419
PBT/AHP15	472	476	16.1	409
PBT/AHP10/MPP5	388	381	15.6	410
PBT/AHP10/MC5	345	342	15.4	411
PBT/AHP20	416	417	14.8	406
PBT/AHP15/MPP5	347	344	14.1	409
PBT/AHP15/MC5	325	320	13.9	408

HRC: heat release capacity, ±5 J/g·K; PHRR: peak of heat release rate, ±5 W/g; THR: total heat release, ±0.1 kJ/g; T_{PHRR}: Temperature at PHRR, ±1°C.
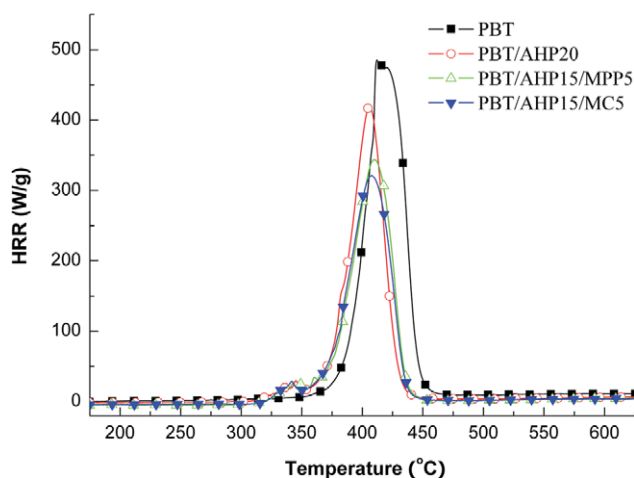
Figure 7 Heat release rate (HRR) curves of the investigated composites from microscale combustion calorimetry. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 FTIR spectra of residues from PBT/AHP20, PBT/AHP15/MPP5 and PBT/AHP15/MC5 after LOI tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

T_{PHRR}. On the contrary, the addition of AHP reduces the T_{PHRR}, indicating a different mechanism.

When AHP and melamine derivatives are combined in PBT, all the MCC data are further reduced (Table IV). From Figure 7 and Table IV, it can be seen that the PHRR values decrease from 485 W/g for neat PBT to 344 W/g for PBT/AHP15/MPP5 with a reduction of 29%, and to 320 W/g for PBT/AHP15/MC5 with a reduction of 34%, respectively. But the PHRR for PBT/AHP20 is only reduced by 14%. At the same time, the THR values for PBT/AHP15/MPP5 and PBT/AHP15/MC5 are reduced by 25 and 26% respectively. The heat release capacity (HRC) is an important single best measure of the fire hazard of a material, which is defined as the maximum heat release rate divided by the constant heating rate in the test.[13,14] From HRC values for all formulations, it is clearly seen that the largest
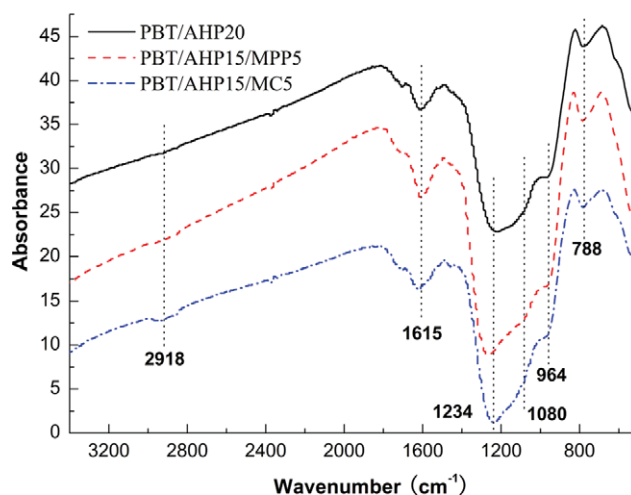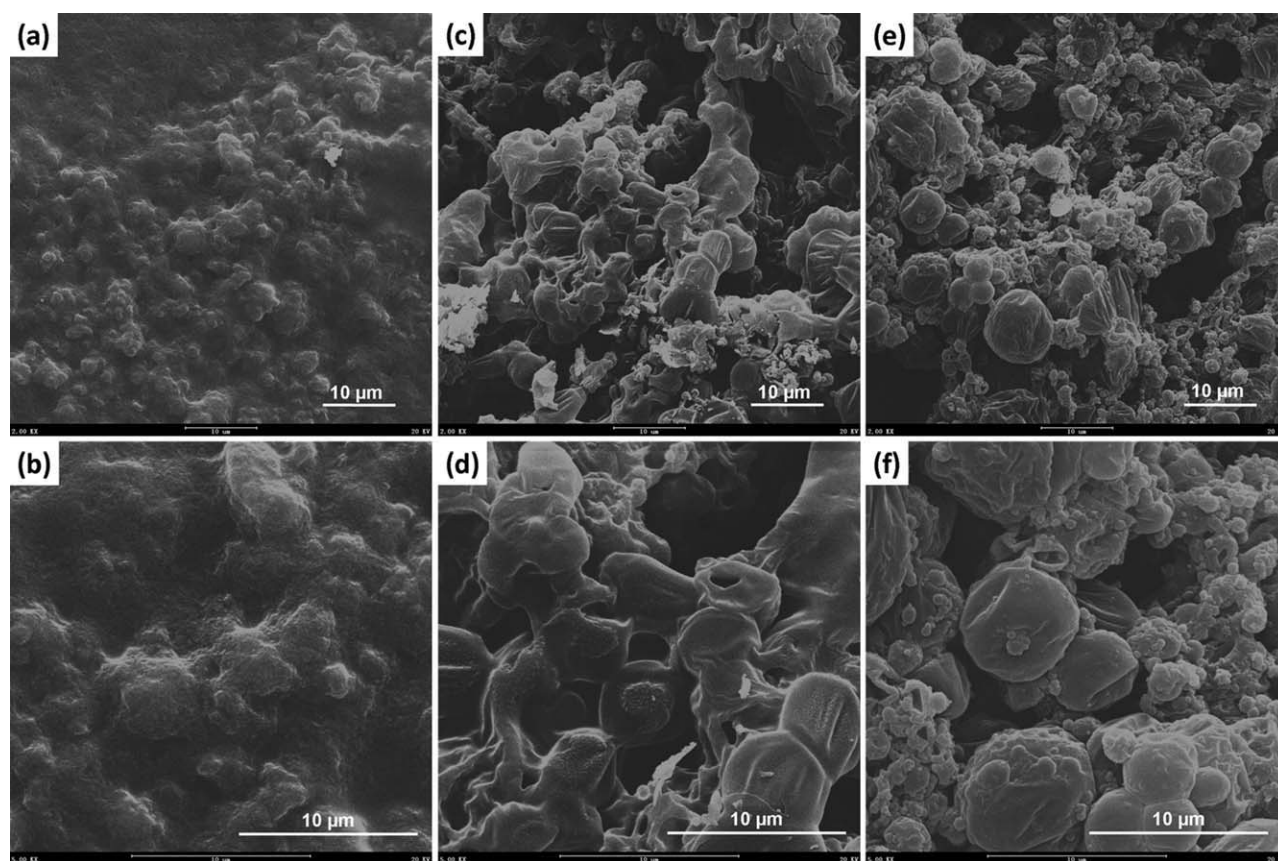
reduction is still attributed to the PBT composites containing AHP and melamine derivatives. At the same time, the introduction of melamine derivatives to PBT/AHP improves the temperature at PHRR. These results substantially demonstrate that the significant reduction of fire hazards for these composites is caused by the synergistic effect between AHP and melamine derivatives. The detailed synergistic mechanism will be discussed in the following parts.

Fire performance

Underwriters Laboratories (UL) 94 and limited oxygen index (LOI) tests were performed to investigate the fire performance of each formulation, which are summarized in Table V. PBT is a flammable polymeric material with a LOI of 20%. In UL 94 test, PBT cannot extinguish itself, and there is a serious dripping in the first application of the flame. The addition of melamine derivatives does not significantly improve the flame class of PBT. When 15 wt % AHP is added, the LOI increases from 20% to 26.5%. In UL 94 test, the specimen for PBT/AHP15 can extinguish after the removal of the first flame application and there is no dripping during the first flame. The composite thus achieves a V-2 classification. As the fraction of the added AHP increases to 20 wt %, the combustion behavior of PBT composite is further influenced. The increased LOI and the improved flame classification in UL 94 testing (V-1 rating) both shows that AHP is an effective flame retardant for PBT. When AHP and melamine derivatives are combined in PBT, the LOI values are further increased, and the flame time in UL 94 tests are significantly reduced. Both of PBT/AHP15/MPP5 and PBT/

TABLE V
Results of UL-94 and LOI Tests for Neat PBT and Its Composites

Sample	LOI	UL-94, 3.2 mm bar		
		t_1/t_2[a] (s)	Dripping	Rating
PBT	20 ± 0.5	BC[b]	Yes/yes	NR[c]
PBT/MPP5	21 ± 0.5	BC	Yes/yes	NR
PBT/MC5	20.5 ± 0.5	BC	Yes/yes	NR
PBT/AHP15	26.5 ± 0.5	19.3/14.5	No/yes	V-2
PBT/AHP10/MPP5	27 ± 0.5	13.8/21.2	No/yes	V-2
PBT/AHP10/MC5	28.5 ± 0.5	9.6/12.2	No/yes	V-2
PBT/AHP20	28 ± 0.5	4.6/19.6	No/no	V-1
PBT/AHP15/MPP5	29 ± 0.5	1.2/8.1	No/no	V-0
PBT/AHP15/MC5	30.5 ± 0.5	1.1/5.2	No/no	V-0

[a] t_1 and t_2, average combustion times after the first and the second applications of the flame.
[b] BC, burns to clamp.
[c] NR, not rated.

Figure 9 SEM images of residues from the investigated composites after LOI tests: (a) and (b) PBT/AHP20; (c) and (d) PBT/AHP15/MPP5; (e) and (f) PBT/AHP15/MC5.

AHP15/MC5 can achieve the V-0 classification. It is indicated that the presence of melamine derivatives in PBT/AHP composites can improve the flame retardancy. The results show that the combined flame retarded action caused by the condensed-phase action and gas-phase dilution effect is similar with the intumescent flame retardancy mechanism, which is a novel combination to enhance the fire resistant performance of PBT matrix.

Residue analysis

To further study the improved flame retardancy, the outer chars of optimized formulations from LOI tests were analyzed by means of FTIR as shown in Figure 8. In fire residues for PBT composites (PBT/AHP20, PBT/AHP15/MPP5, and PBT/AHP15/MC5), aromatic groups are all detected. The peaks at 1615 cm^{-1} and 788 cm^{-1} are attributed to the C=C and C—H vibration of aromatic ring, respectively. It is indicated that carbon residues containing aromatic structure for these composites are remained after LOI test. In comparison with PBT/AHP20, the FTIR spectra for PBT/AHP15/MPP5 and PBT/AHP15/MC5 have no fundamental change between 964 cm^{-1} and 1234 cm^{-1}. The peaks around 1080 and

964 cm^{-1} are attributed to symmetric and asymmetric stretching vibration of P—O bonds.[15,16] The absorption band around 1234 cm^{-1} probably corresponds to the stretching vibration of C—O bonds in ester groups, but the characteristic band around 1720 cm^{-1} of C=O stretching vibration does not appear, indicating the absence of ester groups. In combination with the presence of aromatic compounds in the char, it could be concluded that the peak at 1234 cm^{-1} should be assigned to C—O stretching vibration for P-O-Φ structure, where Φ represents an aromatic group.[17,18] The results demonstrate that the solid product form the initial degradation of AHP, $Al_2(HPO_4)_3$, potentially reacts with aromatic products of PBT leading to the formation of stable residues with P-O-Φ structure. At the same time, the absorption band around 2918 cm^{-1} corresponding to the stretching vibration of alkyl groups occurs in the FTIR spectra of PBT/AHP15/MPP5 and PBT/AHP15/MC5. It is indicated that the char layers for the two composites are more effective to protect the polymer substrate during the combustion compared with PBT/AHP20.

The outer chars of the three composites were also analyzed by means of SEM (Fig. 9). The appearance of PBT/AHP20 char residues shows that the char

layer is compact both in the low and high magnification images, as shown in Figure 9(a,b). From the SEM images of the char residues for PBT/AHP15/MPP5 and PBT/AHP15/MC5 [Fig. 9(c–f)], it is obviously seen that there are amounts of bubbles on the surface. Like intumescent system, MPP and MC in the current flame retardant system play a role of blowing agent resulting in the formation of bubbles. The fact that few broken bubbles present in the outer char layer indicates that the shell of bubbles containing P-O-Φ structure is so tough that it is difficult for gas products to escape. Based on the appearance of char residues, it can be concluded that numerous flammable or toxic volatiles during the degradation or combustion of PBT composites are inhibited by the formed bubbles. As a result, the flammability is retarded due to the reduction of combustible gases. Meanwhile, the mechanism analysis is in strong agreement with the combustion testing and thermal degradation analysis.

CONCLUSIONS

Halogen-free poly(1,4-butylene terephthalate) (PBT) composites were fabricated using ecofriendly flame retardants, aluminum hypophosphite (AHP) and melamine derivatives (melamine polyphosphate and melamine cyanurate) through melt blending process. Microscale combustion calorimetry and thermal gravimetric analysis/infrared spectrometry (TG-IR) technique were used to investigate the potential fire hazards of various PBT composites. For the PBT composites with the incorporation of AHP and melamine derivatives, the heat release capacity (HRC) which is an indicator of a material fire hazard was significantly reduced, and the intensities of a variety of combustible or toxic gases detected by TG-IR technique were remarkably decreased. Moreover, a loading of 20 wt % flame retardant mixture fulfilled the PBT composites high limited oxygen index and V-0 classification in UL 94 testing. Thermal analysis and residue characterization revealed that the flame retardancy of PBT composites is improved by the condensed-phase action of AHP and the gas-phase dilution effect of MC, which is similar with traditional intumescent flame retardant mechanism.

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