Preparation, Characterization and Properties of a Halogen-Free Phosphorous Flame-Retarded Poly(butylene terephthalate) Composite Based on a DOPO Derivative

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ABSTRACT: A phosphorous flame retardant (DOPO-MAH) was synthesized through the reaction between of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and maleic anhydride (MAH) and confirmed by FT-IR, ^{1}H NMR, and ^{31}P NMR techniques. The obtained flame retardant was then melt blended with poly(butylene terephthalate) (PBT) to prepare flame retardant PBT/DOPO-MAH composites. The composites were characterized by LOI, UL-94, and mechanical tests as well as scanning electron microscopy, thermogravimetric analysis, and differential scanning calorimetry analysis. On adding 20 wt % DOPO-MAH, LOI increased from 20.9 to 25.7 and the UL-94 V-0 rating was achieved, whereas the tensile and flexural properties were notably improved. Torque-time profile during the melt blending and intrinsic viscosity of the composite indicated that DOPO-MAH acted as both flame retardant and chain extender for the PBT matrix. The results showed that PBT/DOPO-MAH composite is a promising material for its good comprehensive properties. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1301–1307, 2013

INTRODUCTION

Poly(butylene terephthalate) (PBT) is an important thermoplastic polyester, which has high heat resistance, outstanding mechanical strength and toughness, excellent electrical insulation properties, and good surface appearance.[1] It is often used for insulating parts in the electrical and electronic industries, for example, lamp holder, switches, circuit breakers, and motor casings where required high flame retardant properties. Neat PBT is highly combustible, so it is necessary to improve its fire retardant properties to meet the fire safety requirements. Typical flame retardant additives for PBT includes: halogenated systems, organic or inorganic compounds containing phosphorus, inorganic metal hydroxides, boron, and nitrogen compounds and combinations thereof.[2] Halogen-containing additives were found to be very efficient flame retardants in PBT; however, they have some negative aspects, in particular the emission of toxic and corrosive gases and smoke, during combustion or high temperature processing.[3,4] So, it is necessary to promote the development of halogen-free flame retardant additives that has been promoted by what mentioned above. In particular, phosphorus-based flame retardants are considered to be the preferred halogen-free alternatives.[5–10] Generally, there are two kinds of flame retardant used to improve the flame retardant properties of PBT. First, additive flame retardants are mixed into the polymer material. Second, reactive flame retardants are directly reacted into the polymer chain. The first method often suffers from the drawbacks like additives exude onto the surface of materials, impart discoloration of the molded products and the deterioration of mechanical or other physical properties of PBT.[2] The use of reactive flame retardants can overcome some of these drawbacks, but the synthetic methods of polymeric materials need to be improved.[4]

DOPO (9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and its derivatives have been used as novel phosphorus flame retardants in polymeric materials, such as epoxy resins and polyesters to improve their flame retardancy.[2,11,12] DOPO and its derivatives were found to be effective flame retardant for polyesters, in most cases they acted as a reactive flame retardant by their introduction during the synthesis of polyesters. In this article, we synthesis a novel derivative of DOPO by the addition reaction between DOPO and maleic anhydride (MAH). The compound named DOPO-MAH, has reactive anhydride groups, which can react with the hydroxyl groups of PBT. The synthesis, characterization of DOPO-MAH, its compounding with PBT and torque–time profiles during compounding, and flame retardant property, intrinsic viscosity, thermal properties, and
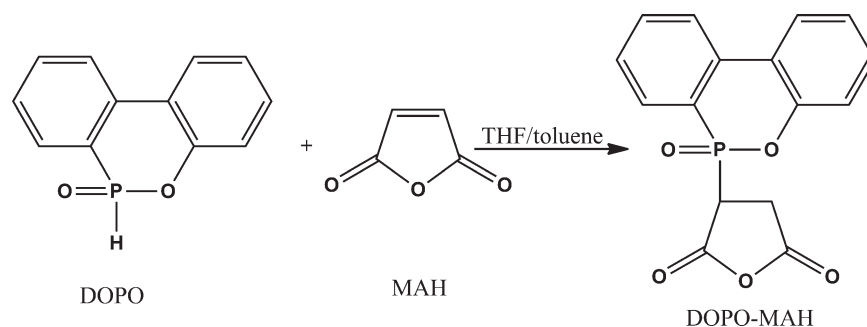
Scheme 1. Synthesis of DOPO-MAH.

mechanical properties of PBT/DOPO-MAH composites were investigated. The resulting PBT/DOPO-MAH composites are expected to be a permanent flame retardant material, where DOPO-MAH can partly react with PBT.

EXPERIMENTAL

Materials

PBT (1100-211M) used in this article was obtained from Taiwan Changchun Petroleum & Chemical. DOPO, a commercial product, was purchased from H&G Chemical, Jiangsu, China. MAH, toluene, tetrahydrofuran (THF) and ethanol were all of analytical grade and used without further purification.

Synthesis of DOPO-MAH

The synthesis of DOPO-MAH is illustrated in Scheme 1 and the detail is as follows: 216.0 g (1.0 mol) of DOPO, 400.0 mL of toluene and 400.0 mL of THF were introduced into a round-bottom glass flask equipped with a gas inlet, a condenser, and a mechanical stirrer. The mixture was heated to the reflux state and stirred simultaneously under a nitrogen gas atmosphere. When DOPO dissolved completely, 98.0 g (1.0 mol) of MAH was added to the reactor in several portions within 1 h. The reaction mixture was maintained at the reflux state under stirring for 6 h under a nitrogen gas atmosphere in order to ensure completion of the reaction. After cooling to room temperature, the precipitate was collected by filtration, washed with THF and

ethanol (1:1, V/V) mixture for three times, and finally dried under reduced pressure overnight at 120°C. The obtained DOPO-MAH product was a white powder. An instrumental analysis on the powder was carried out by Fourier transform infrared (FTIR) spectroscopy using a Nicolet 6700 spectrometer (Nicolet Instrument Company, USA), ^{1}H and ^{31}P nuclear magnetic resonance (^{1}H/^{31}P NMR). ^{1}H NMR spectrum was obtained with a Bruker Avance 400 (Bruker BioSpin AG, Switzerland) using DMSO-d6 as solvent with TMS as internal standard and ^{31}P NMR spectrum was obtained with a Bruker Dmx 300 (Bruker BioSpin AG, Switzerland) using CDCl$_3$ as solvent with H$_3$PO$_4$ as internal standard. Figure 1 shows the FTIR spectrum of DOPO-MAH. The absorption around 1266 cm^{-1} corresponds to vibration with P=O, which is characteristic of phosphoric compounds. The DOPO-MAH also showed strong absorptions around 753 cm^{-1} corresponding to P–O–C (aromatic) stretching, the P–C stretching absorption around 1477 cm^{-1}, the C=O absorption around 1785 cm^{-1} and the aromatic C–H absorption around 3066 cm^{-1}. Figure 2 shows ^{1}H NMR spectrum of DOPO-MAH that reveals the CH peak at 6.57 ppm, the CH$_2$ peak at 6.33 ppm and Ar-H peaks at 7.03–8.23 ppm. Furthermore, DOPO-MAH exhibit a single peak at 21.56 ppm in the ^{31}P NMR spectrum (Figure 3), indicating both the purity and structure of the obtained compound.

Compounding

PBT and DOPO-MAH were dried at 105°C overnight before compounding. The PBT/DOPO-MAH were prepared by melt
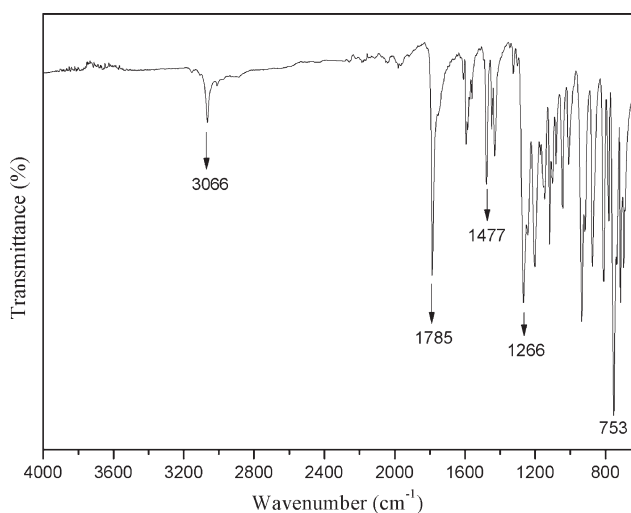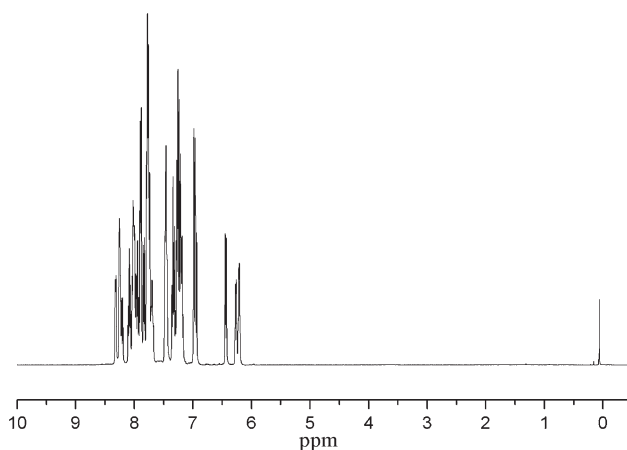

Figure 1. The FTIR spectrum of DOPO-MAH.

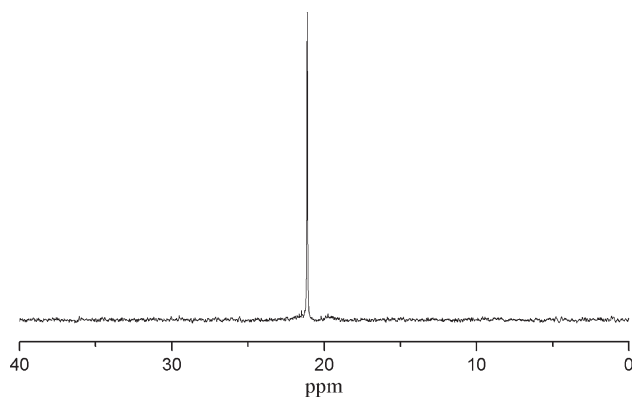**Figure 2.** The ^{1}H NMR spectrum of DOPO-MAH.

Figure 3. The ^{31}P NMR spectrum of DOPO-MAH.

blending PBT and DOPO-MAH using an HAAKE Polylab OS RheoDrive 7 (Thermo Fisher Scientific, Germany) at 245°C with a low rotor speed of 50 rpm for the first 1 min for preheating, then with a high rotor speed of 100 rpm for another 6 min for complete mixing. Torque data were recorded during the melt blending. The PBT/DOPO-MAH composites were prepared in five formulations, as listed in Table I. SEM observation (micrographs not shown) indicated that DOPO-MAH was uniformly dispersed in the PBT matrix and no evident agglomeration was present. Pure PBT was processed with the same mode as the reference. Specimens for mechanical properties test were prepared according to per standard using the HAAKE mini-jet II piston injection molder (Thermo Fisher Scientific, Germany) at a melt temperature of 270°C and mold temperature of 80°C. The injection pressure was 850 bars in each case.

Combustion Test
The combustion behaviors of PBT/DOPO-MAH were characterized by the limited oxygen index (LOI) and vertical burning according to the standard ASTM D2863 and UL-94, respectively. The LOI values were measured on an HC-2 LOI instrument (Jiangning Analysis Instrument Company, China) with sheet dimensions of $130 \times 6.5 \times 3.0$ mm^3. The test was based on the determination of the percentage of oxygen in a gas mixture (O$_2$ and N$_2$), which was just sustaining the burning of 50 mm length of a sample for 180 s. UL-94 test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) with sheet dimensions of $130 \times 13.0 \times 3.2$ mm^3.

Intrinsic Viscosity
The intrinsic viscosities of PBT/DOPO-MAH composites were measured with an Ubbelohde viscometer (Beijing Glassware Plant, Beijing, China) at a concentration of 0.5% (w/v) in phenol/1,1,2,2-tetrachloroethan (w/w = 60:40) solution at 25°C. The solution was filtered before testing. From the flow time of the pure solvent (t_0) and of PBT solutions (t), the relative (η_r) and intrinsic ($[\eta]$) viscosities were calculated using the following equations:

$$\eta_r = t/t_0 \qquad (1)$$

$$[\eta] = \frac{0.25 \times (\eta_r - 1 + 3\ln \eta_r)}{c} \qquad (2)$$

where c is the concentration of PBT in the solution (0.5 g/mL).

Thermogravimetric Analysis
Thermogravimetric analysis (TGA) was carried out using a PE Pyris 1 thermogravimetric analyzer (Perkin Elmer, USA). Samples of 3–4 mg were heated in an open Pt pan from room temperature to 600°C at a heating rate of 20°C/min, under a constant nitrogen flow of 20 mL/min.

Differential Scanning Calorimetry
Differential scanning calorimetry (DSC) measurements were performed by a TA Q2000 DSC apparatus (TA instruments, USA) in sealed Tzero^{TM} aluminum pan under nitrogen atmosphere. DSC was calibrated with pure indium standard, using a cooling attachment RSC 90 to satisfy the temperature changes. The samples were first heated from room temperature to 270°C at a rate of 20°C/min, kept for 5 min to eliminate the thermal history, and cooled at a rate of 20°C/min to 0°C. After 5 min, the cooled samples were again heated at a rate of 20°C/min to 270°C. The melting temperature (T_m) and crystallization temperature (T_c) were defined at the maxima of the DSC peaks. The corresponding enthalpy changes, ΔH_m and ΔH_c were obtained from peak area integration. The degree of crystallinity (X_c) for PBT was calculated using 140 J/g as the melting enthalpy (ΔH_m^0) for 100% crystallized PBT with the following equation:[14]

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \qquad (3)$$

Mechanical Properties
Mechanical properties of the PBT/DOPO-MAH composites were measured on a universal testing machine (Model 3365, Instron Engineering Corporation, Canton, MA) at room temperature. The ensile test was carried out according to ISO 527-2 using an extensometer at a cross-head speed of 5 mm/min whereas the flexural test was according to GB/T 9341 at a cross-head speed of 2 mm/min. A minimum of five samples were tested for each condition. The average and standard deviation of obtained values were calculated.

RESULTS AND DISCUSSION

Torque–Time Profiles during Melt Blending and Intrinsic Viscosity
During the preparation of PBT/DOPO-MAH composites in the internal mixer, the melt torque of the mixtures was recorded.

Table I. Formulations of PBT/DOPO-MAH Composites and Results of UL-94 and LOI tests

Sample	Formula (wt %)		LOI	UL-94		
	PBT	DOPO-MAH		Ranking	Dripping[a]	t_1/t_2[b]
PBT-0	100	0	20.9	HB	–	–
PBT-5	95	5	23.7	HB	–	–
PBT-10	90	10	25.6	V-2	Y/Y	10/16
PBT-15	85	15	25.8	V-1	Y/Y	6/15
PBT-20	80	20	25.7	V-0	N/Y	2/8
PBT-25	75	25	25.8	V-0	N/Y	1/2

[a] Y/N stands for yes/no dripping at the first/second flame application.
[b] Average combustion time (s) of five samples after the first/second flame application.
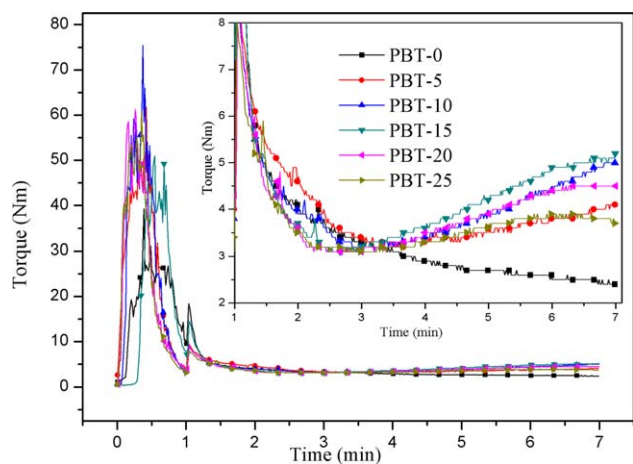
Figure 4. Torque–time curves of PBT/DOPO-MAH composites during melt blending. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The data are drawn as a function of mixing time and shown in Figure 4. In the preheating stage (the first minute), the torque revealed a sharp peak for all the samples because the components had experienced a sudden melting process, meanwhile the mixing underwent gradually after melted as the temperature increased until reaching the fixed value (245°C). At the end of the first minute, the rotor speed was turned from 50 to 100rpm in order to ensure a complete mixing, another sharp peaks of the melt torque appeared for all the samples.

The torque required to process a polymer is in turn a direct measure of the molecular weight of the polymer, because it is proportional to the intrinsic viscosity of the polymer. It is believed that the torque may be used to indicate the degradation or crosslinking of a polymer during melt processing.[13] In the mixing stage, the torque kept a continuous decreasing for the pure PBT system, obviously because of mainly attributed to the degradation of the macromolecules. It is observed that the melt torque reached ca. 2.5 Nm by the end of processing. With the introduction of DOPO-MAH, after a minimum value reached at the third minute, the torque slowly increased until the end of the composite preparation. Such an interesting phenomenon may be attributed to the chemical reaction between

the anhydride groups of DOPO-MAH and terminal hydroxyl groups of PBT matrix (Scheme 2)[15]; in that reaction, the DOPO-MAH molecules acted like a chain extender to the macromolecules. From Figure 4, it is observed that the final torque of PBT-10 and PBT-15 (containing, respectively, 10 and 15 wt % of DOPO-MAH) increased most rapidly and reached a high value of ca. 5.0 Nm, which is double to the pure PBT system. Because of the low reactivity between DOPO-MAH and PBT, less mount of DOPO-MAH may not be sufficient to completely react with PBT, the unreacted PBT would still undergo partial degradation; therefore, the torque increased little for composites with low DOPO-MAH content. At high content, DOPO-MAH may be excess, which could act as a plasticizer to the composite, thus the torque of the composites increased less, too.

The thermal degradation and chain extension were competitive with each other during the melt blending of PBT and DOPO-MAH. The former reduced the melt torque, whereas the latter caused increase of torque. When the chain extender DOPO-MAH was consumed gradually until exhausted completely, the thermal degradation of PBT kept progressing, the melt torque would reach a maximum value. As shown in Figure 4, when the mixing time was near to the seventh minute, the melt torque seems to reach a plateau. That is to say, the melt blending could not be conducted for a longer period; otherwise the performances of the composites would be deteriorated.

The intrinsic viscosity of PBT/DOPO-MAH composites is shown in Figure 5. It can be seen that the intrinsic viscosity of PBT-0 is much lower than the raw PBT, indicating that the degradation of PBT was occurred during the mixing process. The tendency of intrinsic viscosity of PBT/DOPO-MAH composites is quiet similar to the torque obtained at the end of melt blending. This phenomenon confirmed the chain extension of PBT by DOPO-MAH (Scheme 2).

Flame Retardant Property

The flame retardant property of PBT/DOPO-MAH composites was evaluated by limiting oxygen index (LOI) and vertical burning test (UL-94) compared with neat PBT, as showed in Table I. Neat PBT is a highly combustible material as confirmed by the LOI value of 20.9% and HB classification (the lowest UL-94 rating), as the specimens burnt with flammable dripping during
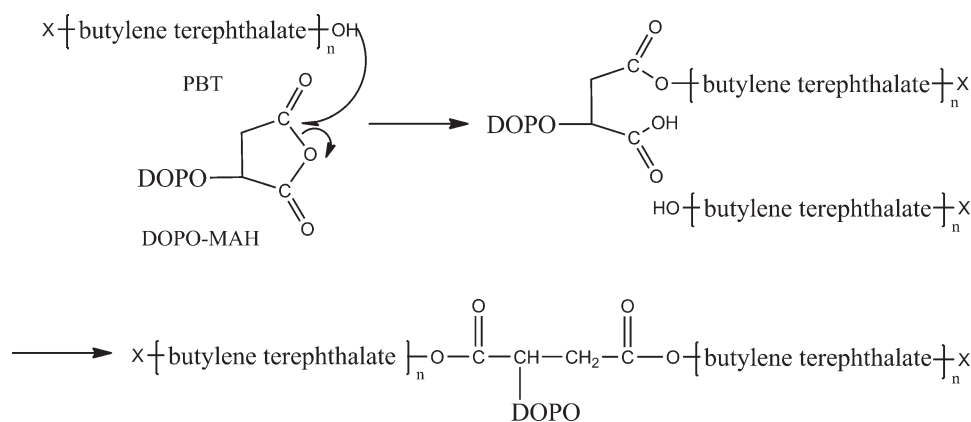
Scheme 2. Chain extension reaction between DOPO-MAH and PBT end groups.
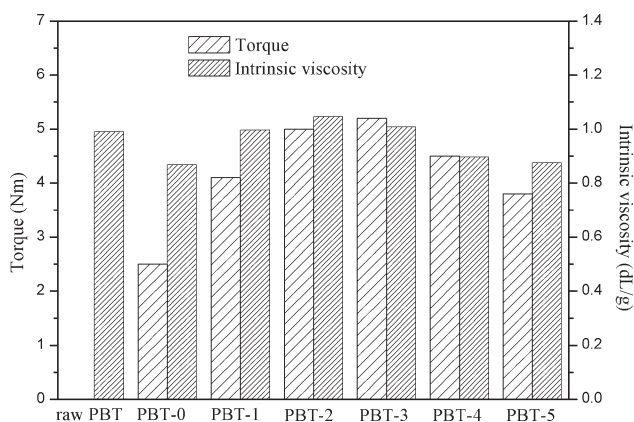
Figure 5. Final torque and intrinsic viscosity of PBT/DOPO-MAH composites.

the test. With the addition of 10 and 15 wt % DOPO-MAH in the composite, the LOI increased from 20.9% to 25.6% and 25.8%, respectively. However, in the UL 94 test, PBT-10 and PBT-15 only reached, respectively, V-2 and V-1 grades while all specimens dripped at the both flame applications. As the

Figure 6. TGA curves of DOPO-MAH and PBT/DOPO-MAH composites at heating rate at 20°C/min in N₂ atmosphere: (a) mass loss curves and (b) DTG curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fraction of the DOPO-MAH increases to 20 and 25 wt%, the composite reached the highest V-0 ranking in UL 94 test with some drips occurred only at the second flame application; however, the LOI value did not increase anymore. It suggests that there is no close correlation between LOI value and UL 94 test.[16,17] When the DOPO-MAH content is up to 25 wt % in PBT, as shown in Table I, the PBT-25 composite shows very short combustion time in UL 94 test: the flame extinguished almost instantly as the source of ignition removed.

Thermal Stability

In order to disclose the flame retardant properties of DOPO-MAH, we detected thermal weight loss curves of all the samples by TGA, as shown in Figure 6. The onset degradation temperature (T_d) of samples, which is evaluated by the temperature of 5 wt % weight loss, the mid-point temperature of the degradation ($T_{50\%}$), the temperature of the maximum weight loss rate (T_{max}) obtained from the DTG curves, and the solid residue at 600°C are listed in Table II. It is observed that all the samples showed a one-step thermal decomposition, according to the unique differential thermogravimetric (DTG) peak. With the addition of DOPO-MAH in PBT matrix, the T_d of PBT/DOPO-MAH composites decrease gradually with the loading of the DOPO-MAH, which may be attributed to the fact that the T_d of DOPO-MAH is much lower than that of PBT: when the samples were heated, the decomposition of DOPO-MAH occurred prior to the polymer matrix. The facile thermal decomposition of DOPO-MAH (including reacted with PBT and unreacted when exceed) could create protective barriers to the combustion and therefore, the flame retardant property of PBT/DOPO-MAH composites was improved with increasing the loading of DOPO-MAH.

If there was no interaction between PBT and DOPO-MAH, the thermogravimetric behavior of the composite should be calculated by a linear combination of the TGA results of individual components in the composites:

$$\text{Weight}_{\text{Composite}} = \text{Weight}_{\text{PBT}} \times [\text{PBT}] + \text{Weight}_{\text{DOPO-MAH}} \times [\text{DOPO-MAH}] \quad (4)$$
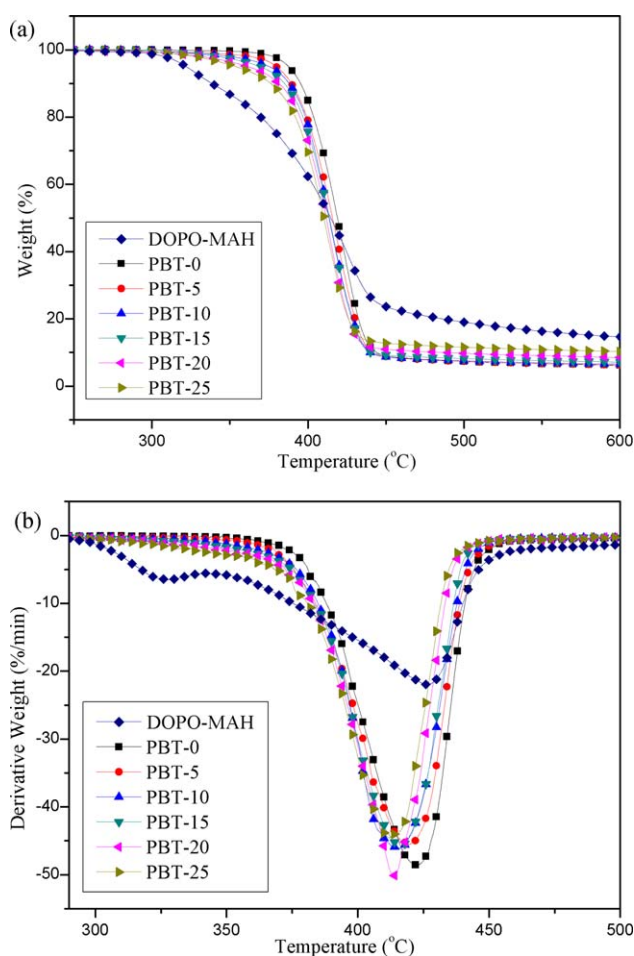
Table II. The Selected Data of TGA Curves of DOPO-MAH and PBT/DOPO-MAH Composites

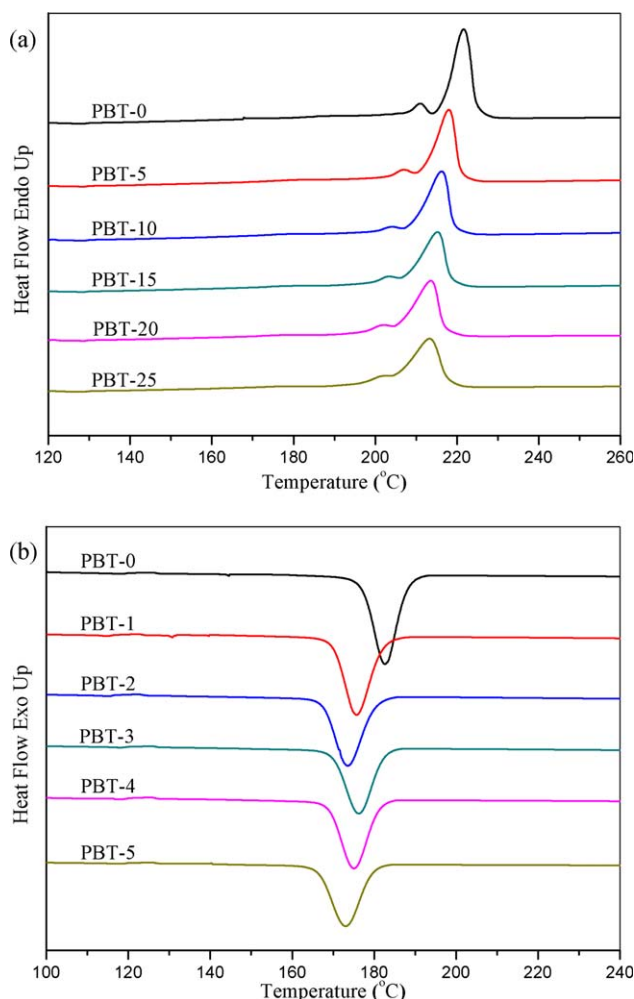| Sample	T_d (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	Residue (wt %)
DOPO-MAH	322.0	414.6	423.4	14.7
PBT-0	387.5	418.8	414.2	6.1
PBT-5	379.8	415.7	419.6	6.6
PBT-5′	384.7	418.7	422.6	6.5
PBT-10	375.4	413.7	415.7	7.3
PBT-10′	381.3	418.6	422.5	7.0
PBT-15	369.3	413.4	416.2	7.8
PBT-15′	376.5	418.6	422.6	7.4
PBT-20	361.7	412.1	412.6	8.5
PBT-20′	370.6	418.4	422.6	7.8
PBT-25	353.8	410.1	411.9	10.3
PBT-25′	363.9	418.3	422.6	8.2

Figure 7. DSC curves of PBT/DOPO-MAH composites: (a) the second heating scan and (b) the cooling scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where Weight$_{PBT}$ and Weight$_{DOPO-MAH}$ are the residual mass of the neat components, [PBT] and [DOPO-MAH] the weight fractions in the composite. The data of the noninteractive representatives to the real composite, denoted with a prime ($'$), are listed in Table II.

Actually, the composites started thermal degradation earlier than the corresponding noninteractive representatives, as the onset degradation temperatures (T_d) are evidently higher than that calculated. However, $T_{50\%}$ and T_{max} are lower while the

Table III. DSC Data of PBT/DOPO-MAH Composites

Sample	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)	T_c (°C)	ΔH_c (J/g)
PBT-0	211.0	221.6	48.9	34.4	185.6	52.8
PBT-5	206.8	217.9	41.1	30.5	180.2	48.3
PBT-10	203.8	216.2	37.4	29.3	178.4	43.7
PBT-15	203.0	215.2	36.3	30.1	179.3	41.4
PBT-20	201.8	213.6	37.0	32.6	178.2	42.8
PBT-25	201.3	213.3	36.6	34.3	176.1	41.2

residues are higher, suggesting that the composites decomposed easily at high temperature and that more flame retardant char formed. This is an additional indication of the interaction between DOPO-MAH and PBT matrix and the chain extension reaction of PBT by DOPO-MAH.

Crystallization Properties

The effect of DOPO-MAH on the melting and crystallization behavior of the PBT was investigated by DSC and the results are illustrated in Figure 7 and Table III.

As shown in Figure 7(a), all of the samples exhibited double melting endothermic peaks during the second heating scan, indicating the presence of two groups of crystals with different morphologies, which could be attributed to the remelting–recrystallization process during DSC scanning.[18] Adding DOPO-MAH lead to reduced melting temperature (T_m) and the T_m value decreased as the DOPO-MAH concentration increased. It may be because of the extension of PBT chains, branches that attach to the polymer chains can be formed during the mixing process.[19] The branches are defects in the crystal lamellae and the chain-extended PBT has a lower melting point. In addition, the unreacted DOPO-MAH might also hinder the motion of PBT molecular chains and the perfection of the PBT crystals. As a result, the crystallization temperature (T_c) and the crystallinity of PBT/DOPO-MAH composites are lower than PBT-0.

Mechanical Properties

The influences of DOPO-MAH on the mechanical properties of PBT composites are shown in Table IV. An increase of DOPO-MAH content in the PBT/DOPO-MAH composites resulted in a great increase in the tensile strength, flexural strength, and flexural modulus, and a big decrease in elongation at break compared with PBT-0. DOPO-MAH with a loading of 15–20 wt % (PBT-15 and PBT-20) effectively increased mechanical properties at the maximum level. This result clearly proved the reaction between DOPO-MAH and PBT. After the reaction, the molecular weight of reacted PBT increased which would improve the mechanical properties of PBT/DOPO-MAH composites. The addition of 25 wt % DOPO-MAH (PBT-25) leads to a little decrease of tensile strength and flexural strength compared to PBT-4, but still shows better mechanical properties than PBT-0. This result may be because of the excess of unreacted DOPO-MAH, which acted as a plasticizer to the composite.

CONCLUSIONS

In this article, the novel phosphorus flame retardant DOPO-MAH was successfully synthesized by DOPO reacted with MAH and characterized by FT-IR, ^{1}H NMR, and ^{31}P NMR. The effects of DOPO-MAH on the flame retardant property of PBT were studied by LOI and UL-94. An increase of LOI was observed and the UL-94 test V-0 rating was achieved by the addition of 20 wt % DOPO-MAH. Torque–time and intrinsic viscosity analysis showed that DOPO-MAH can reacted with PBT matrix as a chain extender. This is a win–win situation both to flame retardant and PBT matrix that a flame retardant can acts as a reactive one by easily melt processing and can give

Table IV. Mechanical Properties of PBT/DOPO-MAH Composites

Sample	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
PBT-0	56.1 ± 0.9	211 ± 50	75.0 ± 0.3	2.15 ± 0.03
PBT-5	62.9 ± 1.2	146.4 ± 20.4	85.0 ± 0.3	2.45 ± 0.01
PBT-10	68.8 ± 0.8	36.3 ± 4.2	86.2 ± 3.0	2.45 ± 0.09
PBT-15	75.3 ± 0.6	21.7 ± 8.0	91.1 ± 0.9	2.56 ± 0.06
PBT-20	74.5 ± 0.2	9.1 ± 0.3	94.3 ± 1.4	2.63 ± 0.01
PBT-25	69.1 ± 1.9	7.4 ± 0.4	92.8 ± 2.6	2.81 ± 0.07

PBT/DOPO-MAH composite a permanent flame retardant property and an improved mechanical properties.

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