

AN S- AND P-CONTAINING FLAME RETARDANT FOR POLYPROPYLENE*

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Abstract A novel charring agent, bis(1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) phenylphosphine sulfide (BCPPS), has been synthesized, and it is combined with ammonium polyphosphate (APP) and melamine phosphate (MP) to impart flame retardance and dripping resistance for polypropylene (PP). The fire performance of the treated PP is investigated by limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter, and the thermal stability and thermal oxidative stability of the composites are studied using thermogravimetric analysis (TG). It has been found that the treated PP with the optimal flame retardant formulation of APP:MP:BCPPS = 12:6:12 (weight ratio, formulation 10) gives an LOI of 31.3 and UL-94 V-0 rating. The results from cone calorimeter indicate that both the heat release rate (HRR) and the total heat evolved (THE) of IFR-PP (formulation 10) decrease significantly compared with those of neat PP. The TG result shows that the IFR-PP (formulation 10) has a high yield of residual char at high temperature. FTIR is used to investigate the residue of the treated PP that degrades at 400°C for different time. The compact outer surface and the shaggy inner surface can be observed from the SEM graph of the residual chars after LOI test, which form a much better barrier for the transfer of heat and fuel during combustion and show good flame retardancy. Moreover, the treated PP and its residue are investigated by XPS analysis.

Keywords: Polypropylene; Intumescent; Flame retardant; Cone calorimeter; Thermal analysis.

INTRODUCTION

Natural and synthetic polymer materials are being used in many fields. Obviously, the demands for polymers are expected to increase significantly in the foreseeable future. Polypropylene (PP) as one of the synthetic polymers is widely used because it is easily processed into products of various shapes with strong tensile stress and high strain at break to meet the requirements of versatile and advanced applications. However the flammability of PP is a significant defect and limits the fields of its application, especially in the home, in work locations, on transport facilities and in public places. Therefore, how to improve effectively its flame retardancy becomes an urgent situation.

Generally, this problem can be solved by using flame-retardant additives, such as halogenated compounds in synergistic combination with antimony trioxide^[1]. However, in the recent years, the usage of these flame retardants has been forbidden gradually because of the possible formation of extremely toxic halogenated dioxins or dibenzofurans, which may be associated with other serious health effects including cancer. In the search for halogen-free flame retardants, intumescent flame retardant (IFR) has received considerable attentions recently^[2–6] because they provide fire protection with minimum of overall health hazard. The intumescence is defined as the swelling of a substance when it is heated, which results from a combination of charring and foaming of the surface of the burning polymer. The resulting foamed cellular charred layer provides a thermal and physical barrier to the underlying material or bulk polymer from the action of the heat flux or the flame.

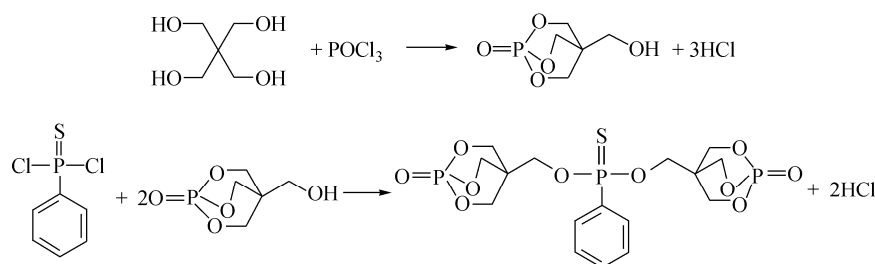
In addition, a number of sulfur-and/or phosphorus-containing flame retardants have been reported^[7, 8].

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However, those kinds of compounds are seldom used as intumescent flame retardants. In this study, a novel sulfur-and phosphorus-containing flame retardant, bis(1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) phenylphosphine sulfide (BCPPS, see Scheme 1) is synthesized successfully and characterized by FTIR and ^1H -NMR. Its flame retardant effects on PP and thermal properties have been discussed. The residues after combustion are investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).



Scheme 1 The synthesis of BCPPS

EXPERIMENTAL

Materials

Polypropylene (1300) was provided by Yanshan Petroleum Chemical Company. (Beijing, China). Phosphorus oxychloride (POCl_3), pentaerythritol (PER), acetonitril and triethylamine were supplied by Changzheng Chemical Reagent Corp. (Chengdu, China). Dioxane which was dried with sodium hydroxide and distilled prior use was provided by Bodi Chemical Reagent Corp. (Tianjin, China). Ammonium polyphosphate (APP) was supplied by Changfeng Chemical Corp. (Shifang, China). Melamine phosphate (MP)^[9] was synthesized by our laboratory. Phenylphosphonothioic dichloride (PPTD), which was distilled before usage, was supplied by Chengdu Weili Flame Retardant Chemicals Industry Co.Ltd. (Chengdu, China). 1-Oxo-4-hydroxymethyl-2, 6, 7-trioxa-1-phosphabicyclo[2,2,2]octane (PEPA) was synthesized according to reference^[10].

Preparation of Bis(1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) Phenylphosphine Sulfide (BCPPS)

A 250 mL three-necked round bottom flask was equipped with a magnetic stirrer, reflux condenser and addition funnel. The flask was charged with 18 g (0.1 mol) PEPA, 10.1 g (0.1 mol) triethylamine and 60 mL acetonitril. Thereafter the mixture was stirred and heated to reflux. Then 10.5 g (0.05 mol) PPTD was added within about 0.5 h. The reaction was kept about 8 h at the same temperature. Successively, the reaction mixture was cooled to room temperature then poured into distilled water and filtered. The solid was washed with water to give 18.3 g (73.5%) white solid.

Preparation of Samples

All samples were prepared on a two-roll mill at the temperature range of 180–185°C for 15 min. After mixing, the samples were hot-pressed under 10 MPa for 5 min at 190°C into sheets of suitable thickness and size.

Measurements

FTIR and ^1H -NMR

Residue samples of intumescent flame-retardant polypropylene (IFR-PP) for the measurement of FTIR spectra were obtained after samples were heated in air at 400°C for different time. The FTIR spectroscopy was studied by using a Nicolet FTIR 170SX infrared spectrophotometer. The ^1H -NMR spectra were recorded on a FT-80A NMR using DMSO as a solvent and TMS as an internal standard.

LOI and UL-94

The limiting oxygen index (LOI) values were measured on an HC-2C oxygen index meter (Jiangning Analysis

Instrument Company, China) with sheet dimensions of 130 mm × 6.5 mm × 3 mm according to ASTM D2863-97.

The vertical burning tests were carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) with sheet dimensions of 130 mm × 13 mm × 3 mm according to ASTM D3801.

Cone calorimeter tests

The signals from the cone calorimeter (Fire Testing Technology Ltd., UK) were recorded and analyzed by a computer system. All samples (100 mm × 100 mm × 6 mm) were exposed horizontally to an external heat flux of 35 kW/m² according to ISO 5660 standard procedures.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on a TA Q500 thermogravimetric analyzer (America) from room temperature to 600°C with a heating rate of 10 K/min under nitrogen and air flow at 60 mL/min, respectively.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) observed on a JEOL JSM-5900LV was used to investigate the outer surface of residues of the IFR-PP system. The residue samples for SEM were obtained after LOI test. SEM graphs of the residual char samples were recorded after gold coating surface treatment.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was recorded by a XSAM80, using Mg K_α excitation radiation, operated at 210 W (14 kV and 15 mA) under a high vacuum between 10⁻⁵ and 10⁻⁶ Pa. High resolution spectra of carbon 1s (C1s), nitrogen 1s (N1s), oxygen 1s (O1s), phosphorus 2p (P2p) and sulfur 2p (S2p) core level for samples were obtained. Binding energies were referenced to the carbonaceous carbon at 285.0 eV.

RESULTS AND DISCUSSION

Synthesis and Characterization of BCPPS

PEPA is a derivative compound of PER with a hydroxyl group in its structure, which is chemically active. So we designed and synthesized a novel flame retardant based on PEPA, which is symmetrical and thermally stable.

Table 1 presents the influence of different acid acceptor on the yield of BCPPS. From Table 1, it can be observed that the yield is only 35.3% when no acid acceptor is used. However, with increasing the alkaline of acid acceptors, an increasing yield is obtained. The yield is 73.5% when triethylamine is used.

Table 1. The influence of different acid acceptors on yield of BCPPS production

Acid acceptor	Temperature (°C)	Time (h)	Yield (%)
None	82	8	35.3
Pyridine	82	8	48.2
Triethylamine	82	8	73.5

The BCPPS was characterized by FTIR spectroscopy (Fig. 1). The detailed results are shown as follows. The absorption band at about 3052 cm⁻¹ corresponds to vibration of benzene-H. Absorption of —CH₂— from PER was observed at about 2957 cm⁻¹. The peaks at 1312 and 1030 cm⁻¹ are assigned to P=O and P—O—C in the phosphate, respectively. The peaks at 872 and 841 cm⁻¹ are assigned to the skeleton vibration of caged bicycle phosphates. Moreover, the absorptions at 743 and 692 cm⁻¹ can be assigned to the vibration of P=S.

Figure 2 shows the ¹H-NMR spectroscopy of BCPPS. The broad resonance corresponding to the protons of benzene ring (a) was observed between δ = 7.57 and 7.90. The peaks from δ = 4.61 to 4.76 are attributed to the —CH₂— protons (b) from the caged bicycle phosphates. The —CH₂— protons (c), which was adjacent to benzene ring, resonated at δ = 3.84 and 4.00.

Based on the above analysis, a conclusion could be drawn that the target product was synthesized successfully.

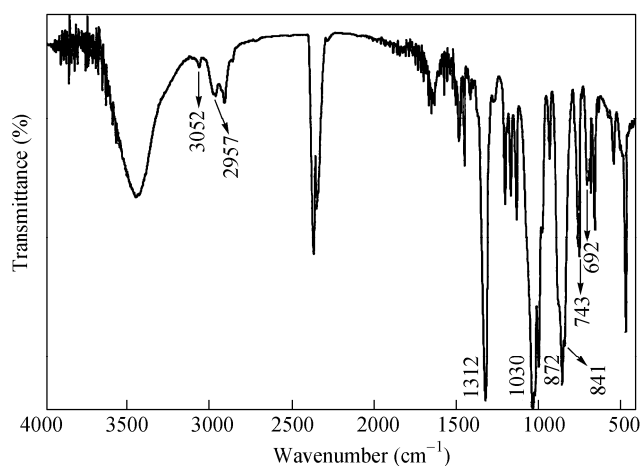


Fig. 1 The FTIR spectrum of BCPPS

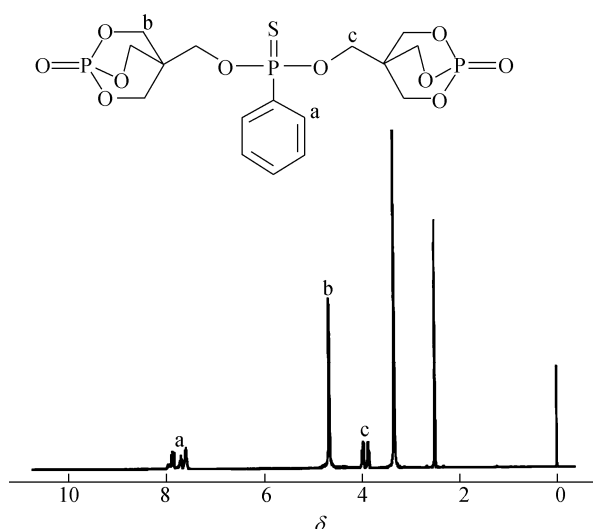


Fig. 2 The ^1H -NMR spectrum of BCPPS

Flammability

A novel compound BCPPS synthesized in this work was used as a charring agent, which was mixed with APP, MP and PP to produce a new intumescent flame-retardant PP (IFR-PP). The limiting oxygen index (LOI) and vertical burning test (UL-94) results were given in Table 2 and Table 3.

Table 2. Effect of APP and MP on flame retardance of PP with a 30 wt% total loading level of additives

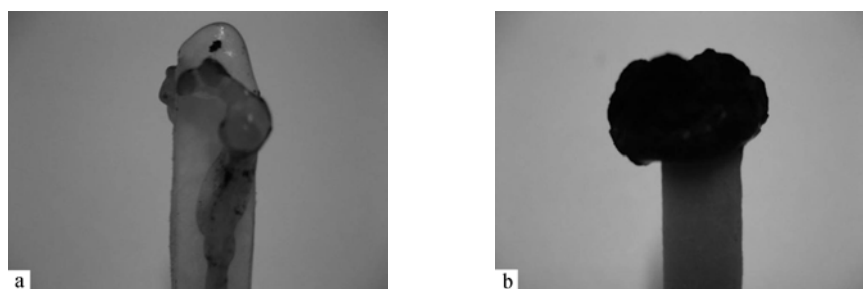
No.	Composition of IFR-PP (%)			LOI	UL-94	
	PP	APP	MP		Ranking	Dripping
1	100	0	0	18.3	Fail	Yes
2	70	30	0	21.5	Fail	Yes
3	70	25	5	23.9	Fail	Yes
4	70	20	10	24.6	V-2	Yes
5	70	15	15	24.4	V-2	Yes
6	70	10	20	22.9	Fail	Yes
7	70	5	25	22.5	Fail	Yes
8	70	0	30	22.0	Fail	Yes

Table 3. Effect of IFR composition on flame retardance of PP with a 30 wt% total loading level of additives

No.	Composition of IFR-PP				LOI	UL-94	
	PP	APP	MP	BCPPS		Ranking	Dripping
9	100	16	8	6	29.8	V-2	Yes
10	70	12	6	12	31.3	V-0	No
11	70	8	4	18	28.4	Fail	Yes
12	70	4	2	24	27.1	Fail	Yes
13	70	0	0	30	22.3	Fail	Yes

Table 2 shows that the LOI value of untreated PP is only 18.3 accompanying with dripping heavily. However, APP or MP with a 30 wt% loading to PP can increase the LOI values to 21.5 and 22.0, respectively. Furthermore, when APP and MP were mixed according to a certain proportion, LOI value can increase gently, and it also dripped heavily due to the absence of charring agent. Based on the result, the best weight proportion of APP to MP is 2:1. Above results also show that APP and/or MP cannot satisfy the flame retardancy of PP.

In order to get good flame retardancy, BCPPS as charring agent is incorporated into the PP/APP/MP composites, and a remarkable improvement of flame retardation is observed (Table 3). When the proportion of APP to MP keeps constant (2:1), it can be seen that LOI value of IFR-PP systems can increase drastically with the increase of BCPPS weight ratio. The LOI value of optimal formulation (formulation 10, APP:MP:BCPPS = 12:6:12) is 31.3, and pass UL-94 V-0 testing, meaning that this IFR composite showed the effective flame retardancy on PP. Meanwhile, no dripping was observed during UL-94 test. Compared with the serious dripping behaviors of pure PP, IFR-PP (formulation 10) showed an excellent anti-dripping property. The difference between the dripping behaviors of PP and IFR-PP (formulation 10) can be observed from LOI testing of the two samples (Fig. 3). Figure 3 clearly demonstrates the anti-dripping effect of BCPPS. It can be seen that the residues of PP are almost all the melt materials after LOI tests (Fig. 3a), while for formulation 10 (Fig. 3b), a coherent and dense char is formed, and the sample shows intumescent carbonaceous chars. The reason for this is that the effective charring agent (BCPPS) can rapidly change the viscosity of melt matrix as encountering fire or heat. However, if the weight ratio of BCPPS goes on increasing, a deteriorated flame retardant effect is observed: the value of LOI decreases and UL-94 test fails.

**Fig. 3** Digital photos of residues after LOI test for (a) pure PP and (b) formulation 10

The above results prove that the ratio of APP: MP: BCPPS is very important in order to obtain good flame retardancy for PP. APP (acid source) catalyzes dehydration and cross-linking reaction of charring agent (BCPPS), and the gases generated by APP or MP foam the carbon layer to act as a physical barrier which slows down heat and mass transfer between the gas and condensed phases^[5, 11].

Cone calorimetry is one of the most effective bench-scale methods to study the flammability of materials. A number of flame-retardant PP composites are investigated by cone calorimetry^[12–17]. Heat release rate (HRR), especially the peak of HRR (PHRR), has been used to evaluate the intensity of fire^[2, 13].

The HRR curves of PP and IFR-PP (formulation 10) at heat flux of 35 kW/m² are shown in Fig. 4. It can be

clearly seen that the pure PP has low resistance to fire, and its HRR increases very fast after ignition. Compared with pure PP, the IFR-PP burns slowly, and its PHRR decreases from 729.6 to 241.4 kW/m². It is worth noticing that the HRR curve of formulation 10 presents two obvious peaks, which is a typical character of intumescent systems. The first peak is assigned to the ignition and to the flame spread on the surface of the materials and then to protection via the intumescent coating when the HRR values become constant. In this time zone, the material is protected by the intumescent char. The second peak is explained by the destruction of the intumescent structure and the formation of a carbonaceous residue^[3, 5]. In addition, the average HRR (Av-HRR) of IFR-PP (formulation 10, 113.9 kW/m²) shows a notable reduction with respect to that of pure PP (324.0 kW/m²).

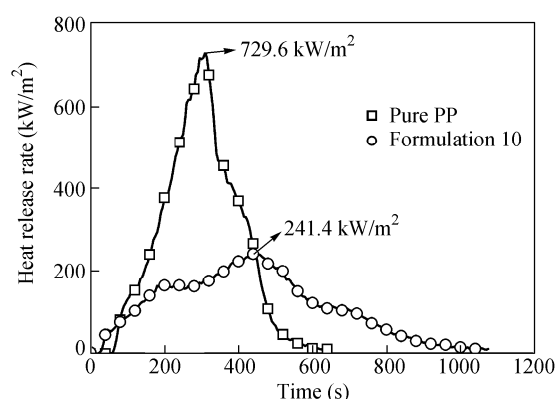


Fig. 4 Heat release rate curves of PP and formulation 10 versus time

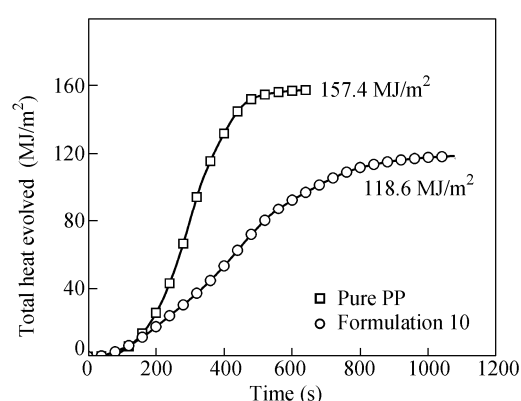


Fig. 5 Total heat evolved curves of PP and formulation 10 versus time

Figure 5 shows the total heat release curves of PP and IFR-PP (formulation 10). Obviously, the total heat evolved (THE) energy of formulation 10 decreases significantly, for example, from 157.4 MJ/m² for pure PP to 118.6 MJ/m² for formulation 10. The lower THE value with respect to prediction indicates that a part of the polymers is not completely burned^[18] because during combustion, an intumescent char forms on the surface of the matrix, which makes a thermal insulation and provokes the extinguishment of the flame, preventing combustible gases from feeding the flame and also isolating the burning material from oxygen^[19].

All the data above (HRR, Av-HRR and THE) indicate strongly that the heat transfer between the flame and the matrix is decreased significantly due to the protection of the efficient char layer, so the flame retardancy is improved.

Thermal Analysis of PP and IFR-PP

Thermogravimetric analysis (TGA) is an effective method to estimate the thermal stability and thermal degradation behavior of various materials. Figure 6(a) shows the TG curves of APP, MP, BCPPS, pure PP and IFR-PP (formulation 10) under nitrogen, it can be seen that PP shows a one-step weight loss whereas APP, MP and BCPPS decompose in two steps. For PP, no residue is formed at 600°C, while for the charring agent BCPPS, the residue is 47.0 wt% at 600°C, which confirms that BCPPS is a very effective charring agent. With the addition of flame retardants including APP, MP and BCPPS, it can be seen that the IFR-PP (formulation 10) exhibits an enhanced thermal stability in comparison with the virgin PP. Namely, a high amount of residues from 441°C to 600°C is generated for IFR-PP (formulation 10).

Figure 6(b) show DTG curves of PP and IFR-PP (formulation 10), which reflects the weight-loss rate of materials. It can be seen that the IFR-PP (formulation 10) shows a lower and wider peak than PP, indicating a slower degradation rate and a stepwise mode instead of a “burst mode”, which may account for the satisfactory flame retardance.

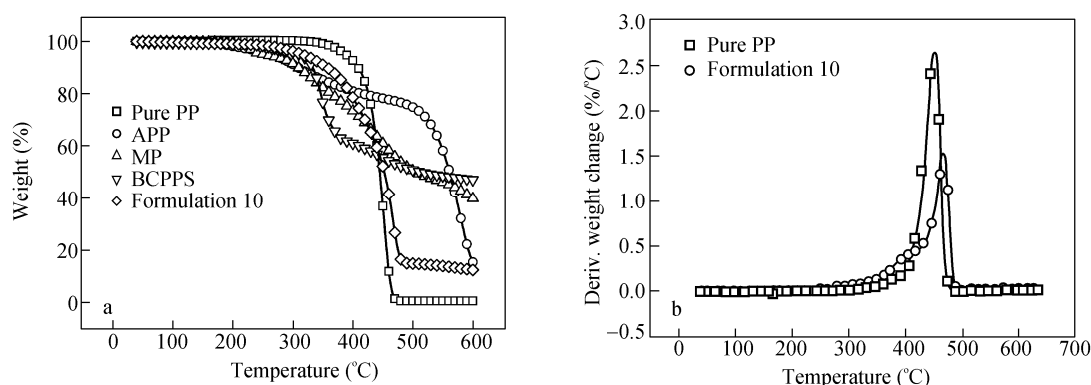


Fig. 6 TG curves of PP, APP, MP, BCPPS and formulation 10 in nitrogen (a) and DTG curves of PP and formulation 10 in nitrogen (b)

The TG curves of APP, MP, BCPPS, pure PP and IFR-PP (formulation 10) under air atmosphere are shown in Fig. 7(a). It is clearly seen that pure PP begins to decompose at 278°C. When the temperature further increases, weight loss increases rapidly and a quantity of volatile is produced until all exhaust at about 390°C at which residue no longer exists. APP is a crucial ingredient of IFR, which acts as an acid source to catalyze the dehydration and cross-linking reaction of BCPPS; at the same time, it also acts as a blowing agent to produce gas to foam the char layer. It degrades by two steps and gives 33.1 wt% residues at 600°C. In addition, when MP is heated, it initially produces more stable melamine pyrophosphate (MPP), and MPP further decomposes to form melamine polyphosphate, melam ultraphosphate, *etc.*^[20]. It can be seen from Fig. 7(a) that BCPPS shows a very good thermal oxidative stability: the onset temperature is 331°C based on 5% weight loss, and the char residue is about 44.7% at 600°C. Furthermore, it can also be found that BCPPS is expandable rapidly when it is exposed to fire or heat.

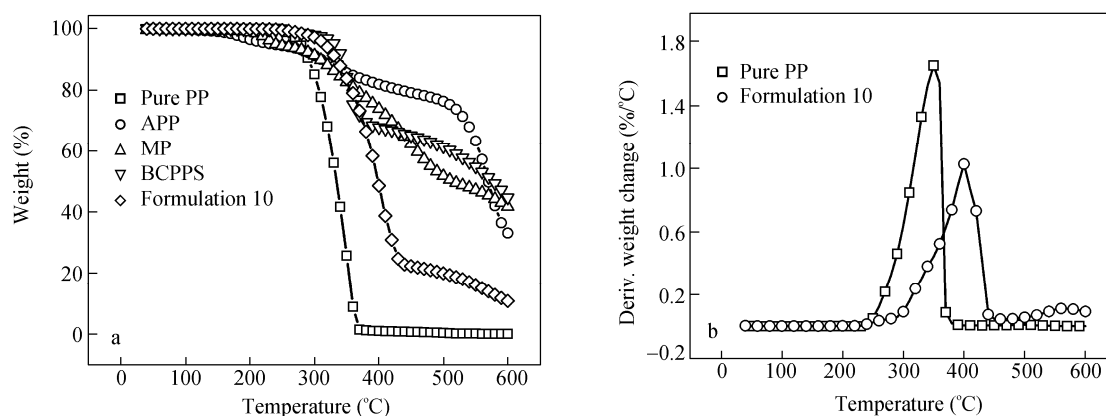


Fig. 7 TG curves of PP, APP, MP, BCPPS and formulation 10 in air (a) and DTG curves of PP, formulation 10 in air (b)

When the additives containing APP, MP and BCPPS are incorporated into PP, the thermal oxidative degradation behavior is changed. It can be seen that the thermal oxidative stability of IFR-PP (formulation 10) is improved significantly in comparison with the virgin PP: a large amount of residues are generated at temperatures ranging from 254°C to 600°C, meaning that there exist some chemical reactions among APP, MP and BCPPS, such as the acceleration of the phosphorylation and the stabilization of polyphosphoric acid by forming bridges or crosslinks between adjacent chains^[21].

Figure 7(b) shows DTG curves of PP and IFR-PP (formulation 10), which reflects the weight-loss rate of

materials. Obviously, the height of the peak of IFR-PP in DTG curves assigned to the major weight-loss stage is lower than that of pure PP, indicating a slower degradation rate. Furthermore, the maximum-decomposing-rate temperature ($T_{\max}$) of IFR-PP (formulation 10) is enhanced by 45 K compared to pure PP, which means that the endothermic reactions take place in IFR charring process and the char layers formed by IFR prevent heat from transferring into the inside of IFR-PP^[6].

FTIR Characterization of IFR-PP Degraded at Different Time

The FTIR spectra of residues from IFR-PP (formulation 10) that are heated in air at 400°C for different time are shown in Fig. 8. From the figure, we can see that the absorptions ranged from 2831 cm^{-1} to 2957 cm^{-1} and 1455 cm^{-1} corresponding to CH_2 or CH_3 vibrations disappear after heated for 30 min. Obviously, this phenomenon may be due to the breaking of CH_2 or CH_3 ^[22]. The absorption of $\text{P}=\text{O}$ is observed at 1252 cm^{-1} ^[13]. The peak at 1079 cm^{-1} is attributed to the stretching vibration of $\text{P}-\text{O}-\text{C}$ ^[13]. The peak at 996 cm^{-1} ($\text{P}-\text{O}-\text{P}$)^[23] becomes gradually evident as time increases, indicating that the char formation exists during the decomposition of the IFR-PP. All the data confirm that the char layer is formed during heating, which serves as a good shelter to protect the underlying matrix so that the flame retardancy of matrix is improved. Unfortunately, we are not able to collect the residue of pure PP because it decomposes completely and releases a large quantity of heat, which is in agreement with the cone calorimetry test. Obviously, this is the reason why the flame retardancy of IFR-PP is much better than that of pure PP.

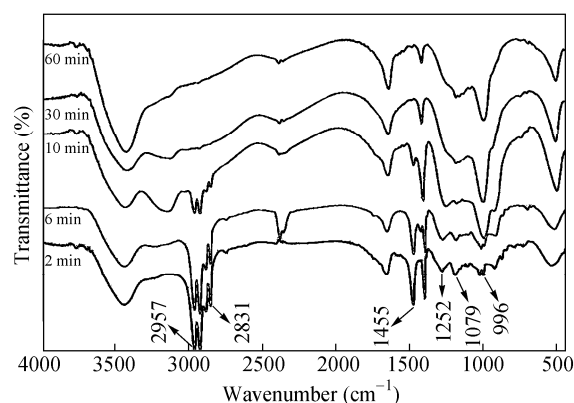


Fig. 8 FTIR of residues of formulation 10 obtained after heated for 2, 6, 10, 30 and 60 min, respectively

SEM Analysis

In order to explore how the structure of intumescent chars influences flame retardancy of PP, the residues of chars left after LOI tests are investigated by SEM. The SEM graphs (a) and (b) in Fig. 9 present the microstructures of the outer surface and the inner surface of the intumescent char residues (formulation 10) after LOI test, respectively. From graph (a), we can see that the outer surface is compact, smooth and tight, moreover, some swollen particles are observed due to the foaming function of gas source. The inner surface in graph (b) is shaggy, and constituted with closed cells and thick framework. All these results indicate that the structure of the chars of both the outer surface and the inner surface provides the resistance of mass and heat transfer and retards the degradation of underlying materials effectively^[24]. Therefore, combustion could not be self-sustained. In addition, the char structure can offer a good shield to prevent melted PP from dripping during combustion, which can ensure excellent flame retardancy.

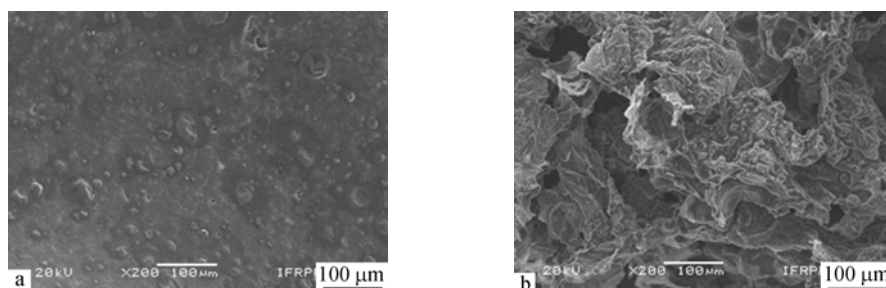
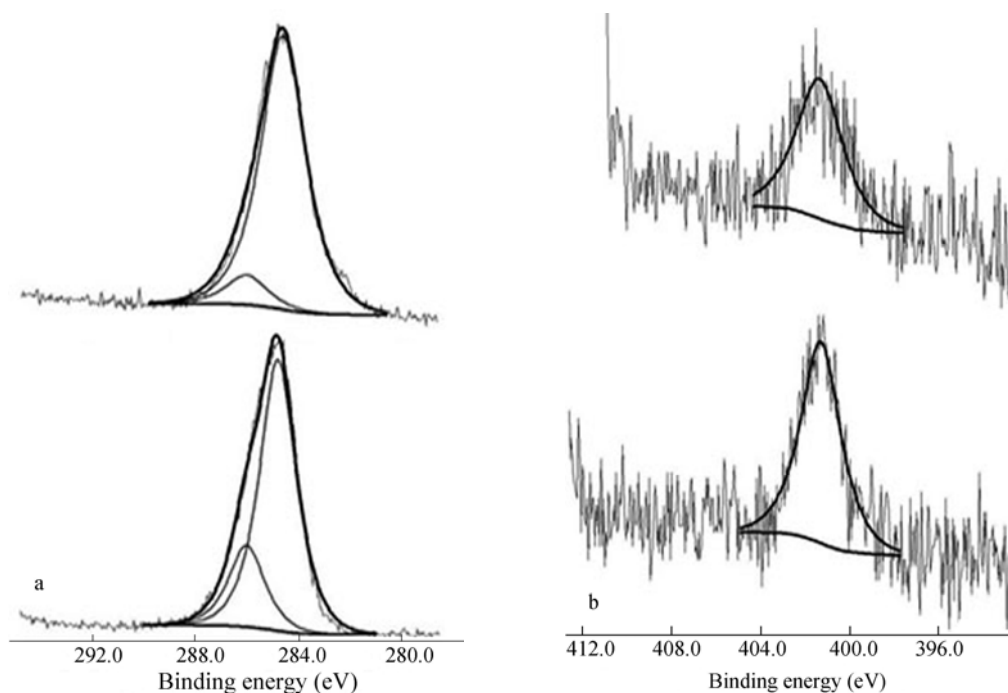


Fig. 9 SEM of intumescent chars (formulation 10, $\times 200$)
a) Outer surface; b) Inner surface

X-ray photoelectron Spectroscopy (XPS) Analysis

In order to pay more attention to the condensed phase, XPS spectra of C1s (a), N1s (b), O1s (c), P2p (d), and S2p (e) of IFR-PP (formulation 10) and its residues after combustion are shown in Fig. 10. In Fig. 10(a), the peak of C1s at 284.8 eV is the contribution of C—C in aliphatic and aromatic species in the materials^[25]. The binding energy of 286.0 eV should be assigned to C—O in C—O—P^[26]. The binding energy of the residue for N1s shifts downward from 401.6 eV to 401.3 eV, compared with that of formulation 10. The band at 401.3 eV could be a result of the formation of quaternary nitrogen and some oxidized nitrogen compounds, as reported in the literature^[27]. Two bands at 531.5 and 532.8 eV are observed from O1s spectra as shown in Fig. 10(c). Since the O1s band is structure-less, it is impossible to monitor the separate contributions of inorganic and organic oxygen^[26]. It is reported that the band at 531.5 eV can be assigned to double bonding =O in phosphate or carbonyl groups^[28], while the band centered around 532.8 eV can be assigned to —O— in C—O—C, C—O—P and P—O—P groups^[29, 30]. Usually the binding energy of P2p of inorganic phosphorus is 130 eV, whereas the P2p peak of sample appears around 134.0 eV. The increase of binding energy demonstrates that the formation of oxidation products of the phosphate species^[31]. Furthermore, compared with that of formulation 10, the binding



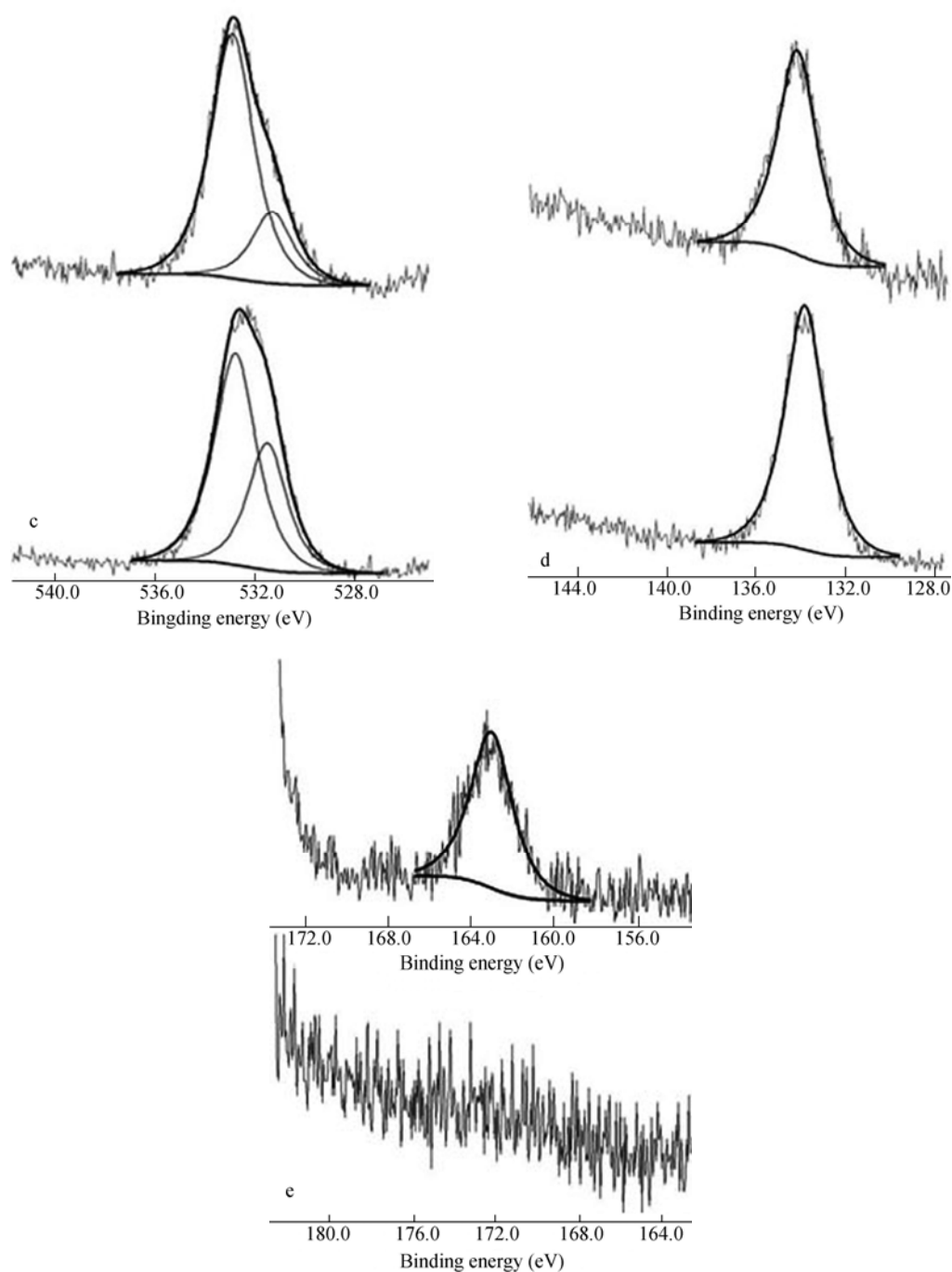


Fig. 10 XPS of formulation 10 (upper) and its residue (lower) after combustion: (a) C1s, (b) N1s, (c) O1s, (d) P2p and (e) S2p

energy for P2p of the residue shifts downwards from 134.2 eV to 133.8 eV. The band of P2p at 133.8 eV can be assigned to PO_3^- and $\text{P}_2\text{O}_7^{4-}$, which is the evidence of the occurrence of dehydration of organic compound^[25, 32]. From Fig. 10(e), we can see that the band of S2p of formulation 10 is at 163.0 eV, corresponding to $=\text{S}^{[32]}$, but no obvious binding energy of sulfur is detected in the residue of formulation 10. The reason for this may be that more sulfur-containing compound formed is covered with intumescent char; and just few amounts remained in

the surface so that they can not be detected by XPS.

The above results confirm that phosphorus and polyphosphorus acid are formed during combustion, which act as dehydration agents to drive formation of the heat-resistant carbonaceous char.

CONCLUSIONS

A novel flame retardant, bis(1-oxo-4-hydroxymethyl-2, 6, 7-trioxa-1-phosphabicyclo[2.2.2]octane) phenylphosphine sulfide (BCPPS) has been synthesized successfully. It can effectively improve the flame retardancy of PP when it is used together with APP and MP. The optimum formulation of IFR-PP system (formulation 10) is 12 wt% APP, 6 wt% MP and 12 wt% BCPPS, and it can obtain a LOI value of 31.3 and reach V-0 rating of UL-94. The results of cone calorimetry tests show that both HRR and THE of IFR-PP (formulation 10) decrease remarkably compared to those of pure PP. TGA curves show that the char yield of IFR-PP is higher than that of pure PP, and the intumescent flame retardant can promote the thermal stability and thermal oxidative stability of IFR-PP. From the analysis of FT-IR and XPS, a conclusion could be drawn that the residual char containing polyphosphoric or phosphoric acid is formed during the combustion. The SEM observations of the residues of IFR-PP confirm the formation of the compact charred layers, which could inhibit the transmission of heat during contacting fire.

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