

Synergistic Effects of Aluminum Hypophosphite on Intumescent Flame Retardant Polypropylene System*

Miao-jun Xu, Jing Wang, Yue-hang Ding and Bin Li**

Heilongjiang Key Laboratory of Molecular Design and Preparation of Flame Retarded Materials, College of Science,
Northeast Forestry University, Harbin 150040, China

Abstract The effects of aluminum hypophosphite (AHP) as a synergistic agent on the flame retardancy and thermal degradation behavior of intumescent flame retardant polypropylene composites (PP/IFR) containing ammonium polyphosphate (APP) and triazine charring-foaming agent (CFA) were investigated by limiting oxygen index (LOI), UL-94 measurement, thermogravimetric analysis (TGA), cone calorimeter test (CONE), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). It was found that the combination of IFR with AHP exhibited an evident synergistic effect and enhanced the flame retardant efficiency for PP matrix. The specimens with the thickness of 0.8 mm can pass UL-94 V-0 rating and the LOI value reaches 33.5% based on the total loading of flame retardant of 24 wt%, and the optimum mass fraction of AHP/IFR is 1:6. The TGA data revealed that AHP could change the degradation behavior of IFR and PP/IFR system, enhance the thermal stability of the IFR and PP/IFR systems at high temperatures and promote the char residue formation. The CONE results revealed that IFR/AHP blends can efficiently reduce the combustion parameters of PP, such as heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and so on. The morphological structures of char residue demonstrated that AHP is of benefit to the formation of a more compact and homogeneous char layer on the materials surface during burning. The analysis of XPS indicates that AHP may promote the formation of sufficient char on the materials surface and improve the flame retardant properties.

Keywords: Synergistic effect; Intumescent flame retardant; Aluminum hypophosphite; Thermal degradation; Polypropylene.

INTRODUCTION

Polypropylene (PP) is one of the most common general plastics and extensively used in industry and daily life, such as building materials, automobile, electronic and electric materials due to its excellent mechanical properties, low density, good performance to cost ratio, ease-processing and good chemical resistance. However, its poor flame resistance restricts its application in many fields, where suitable flame retardant performance is required. Traditionally, the use of bromine-containing flame retardants and antimony trioxide synergistic system is the most effective measure and shows a good ratio of property to price for flame retardant PP, but the use of these flame retardants has been limited because bromine-containing flame retardant produce large amount of smoke and corrosive gas on burning^[1]. Metal hydroxides, such as aluminum hydroxide and magnesium are the other flame retardants for PP, but the high loading would be seriously destroy the mechanical properties of PP^[2].

Intumescent flame retardant (IFR) is a promising halogen-free flame retardant and has aroused a great attention^[3] in recent years due to its merits, such as antidripping property, less smoke and toxic gas released during burning. However, the traditional IFR systems have some drawbacks, such as poor flame retardant

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** Corresponding author: Bin Li (李斌), E-mail: libinzh62@163.com

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efficiency, ease to migration onto the matrix surface during processing and usage, low thermal stability and low water resistance, which are not good for the long-lasting efficiency of the flame retardants^[4, 5]. To solve the shortcomings of IFR, high molecular weight, namely oligomeric or polymeric IFRs have been developed, which provide a good strategy to solve the above problems^[6–8]. In order to enhance flame retardant efficiency, some transitional metal oxides, metal chelates, 4A zeolite, metal compounds and silicon containing compounds were used as synergistic agents to effectively enhance the strength and stability of char layer, stimulate in catalyzing the reactions among IFR components, resulting in the improvement of the flame retardant properties^[9–15].

The aluminum salt of hypophosphorous acid (AHP), the chemical formula is $\text{Al}(\text{H}_2\text{PO}_2)_3$, which has been synthesized on an industrial scale, was reported as an effective flame retardant for PA and PBT, especially for glass-fiber-reinforced products. Zhao *et al.*^[16] reported that AHP was an effective inorganic flame retardant for PA6/GF and investigated the flame retardancy and thermal behavior of the PA6/GF/AP composites, presented the gas-phase and solid-phase flame retardant action caused by AHP. Recently, AHP was reported as an effective flame retardant for GF-PBT^[17, 18]. Yi *et al.*^[19] reported the synergistic flame retardancy between AHP and IFR for PP and AHP produced phosphoric acid at higher temperatures which could promote the carbonization of charring-foaming agent, thus enhance the flame retardancy of PP. However, few literatures reported the effect of AHP on IFR system containing triazine rings and hydroxyl groups, moreover, the mechanism of synergistic effect needs further investigation.

The aim of this research is to combine the fire retarded potential of AHP and triazine IFR system consisting of ammonium polyphosphate (APP) and charring-foaming agent (CFA, a triazine polymer) which was reported in our previous work^[20] to improve the flame retardancy of PP/IFR composites. The flame retardant properties, the formation of charred layers and their microstructure, the synergistic effect of aluminum hypophosphite in PP/IFR systems, the thermal degradation behavior and the flame retardant mechanism of PP/IFR blends were investigated by means of limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetry analysis (TGA), cone calorimeter (CONE), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) *etc.*

EXPERIMENTAL

Materials

PP resin (homopolymer) used in this work with a melt flow index of 3.0 g/10 min was purchased from Daqing Huake Co. Ltd, China. APP (powder, average particle size of 15 μm , GD-101, crystalline from II, $n > 1500$) having soluble fraction in water below 0.2 g/100 mL H_2O was offered by Zhejiang Longyou GD Chemical Industry Co, Ltd. CFA (a triazine polymer) with the average particle diameter of 10 μm was synthesized in our laboratory. APP and CFA were dried in an oven at 105 $^\circ\text{C}$ for three hours. AHP (white power, the average particle diameter of 5 μm) was supplied by Wuhan Chemical New Material Industry Co. Ltd. Nano- SiO_2 (white powder, the average particle size of 50 nm) was supplied by Zibo Hana Co. Ltd. China. PP wax, as a processing aid, was purchased from Daqing Huake Co., China. Antioxidant 1076 was purchased from Ciba Specialty Chemicals, Switzerland.

Preparation of Samples

Intumescent flame retardants (IFRs) consist of 19 wt% CFA, 76 wt% APP and 5 wt% SiO_2 , the weight ratio of APP to CFA is fixed at 4:1. In this research, the flame retardants (FR) included IFR and AHP, the mass ratio of IFR to AHP was kept at 2, 4, 6 and 8. Granules of the flame retardant PP composites were obtained by extruding the mixtures of PP (73 wt%–79 wt%), FR (20 wt%–26 wt%), antioxidant 1076 (0.3 wt%) and PP wax (0.7 wt%) in a twin-screw extruder (D: 20 mm, L/D: 32, model: SLJ-20 Nanjing Jieya Chemical Engineering Equipment Co., China) at a temperature profile of six heating zones (150, 170, 185, 190, 190 and 180 $^\circ\text{C}$) then cutting into pellets. Testing samples were molded by an injector (HTF86X1, Zhejiang Haitian, China) at a temperature profile of five heating zones (210, 220, 220, 220 and 210 $^\circ\text{C}$).

Flame Retardancy Tests

The limiting oxygen index (LOI) is an important parameter for measuring the minimum oxygen concentration to support candle-like combustion of composites. The LOI values were measured on a JF-3 oxygen index instrument (Jiangning, China) with sheet dimensions of 130 mm × 6.5 mm × 3 mm according to ISO 4589-2:1996. The vertical burning ratings were measured on a CZF-2-type instrument (Jiangning, China) with sheet dimensions of 125 mm × 12.5 mm × 0.8 mm according to the American National Standard ANSI/UL 94-2010.

Mechanical Property Tests

Tests of tensile strength, flexural strength and Izod impact of all samples were performed by a Regeer computer controlled mechanical instrument (Shenzhen, China) and a Notched Izod impact instrument (Chengde, China), respectively, according to ASTM standards. At least five specimens were tested for each sample and the average values were reported.

Rheology Property Tests

The rheometric measurements were carried out on an advanced rheometric expansion system (Bohlin Gemini 200) at 190 °C with parallel plate geometry of 8 mm in diameter.

Thermogravimetry Analysis

All thermogravimetry analysis (TGA) tests were carried out by a Perkin Elmer Pyris 1 Thermal Analyzer at a linear heating rate of 10 K·min⁻¹ under pure nitrogen within the temperature range from 50 to 800 °C. The weight of every sample was kept within 2–4 mg.

Cone Calorimeter Test

All Cone data were taken from a Fire Testing Technology cone calorimeter (West Sussex, UK) at an incident heat flux of 50 kW·m⁻² according to ISO 5660-1 standard. The samples (100 mm × 100 mm × 3 mm) were laid on a horizontal sample holder.

Scanning Electron Microscopy (SEM)

SEM was used to examine the morphology of the char residue obtained from cone calorimeter tests using an FEI QuanTa-200 (Eindhoven, Netherlands) SEM. The accelerating voltage was set to 15 kV. The surface of char residues was sputter-coated with gold layer before examination.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out in an ultrahigh vacuum system equipped with a K α hemispherical electron analyzer (ThermoFisher Scientific Company), using a monochromated AlK α source, at a base pressure of 1.0×10^{-8} mbar. C, N, P, O and Al elements were analyzed.

RESULTS AND DISCUSSION

Flame Retardancy

Table 1 presents the changes of LOI values, UL rating and the total combustion time obtained from the UL-94 test based on average burning time of five specimens versus the weight ratio of IFR and AHP for PP/IFR/AHP composites with a total flame retardant loading of 24 wt%. It can be seen that the LOI value of PP/IFR composite is 36.4% and it reaches UL-94 V-0 rating with the samples thickness of 0.8 mm. The LOI values decreased with the incorporation of AHP in PP/IFR composites and the specimens can pass UL-94 V-0 rating when the mass ratio of AHP/IFR is 1:8. The LOI value reaches 33.1% and that total combustion time reaches the least of 4.7 s when the mass ratio of AHP/IFR increased to 1:6. The LOI values gradually decrease with increasing of the content of AHP in flame retardant. The LOI value dramatically decreases to 26.0% and it can't pass any rating with heavily dripping, named no rating when the weight ratio of AHP/IFR is enhanced to 1:2. The vertical testing results indicate that there is an optimum mass ratio of 1:6 where an obvious synergistic effect exists between AHP and IFR. It has been suggested that a suitable acid source/charring agent/foaming agent ratio in the IFR system is very important to its flame retardancy^[4, 5]. The higher concentration of AHP in the flame

retardant PP system may restrain the swelling behavior and carbonization function, destroy the balance between charring function and foaming agent of the PP/IFR/AHP composite, which lead to the decreasing of the flame retardancy.

Table 1. LOI and UL-94 data of flame retardant PP composites with different weight ratios of AHP/IFR

AHP/IFR	LOI (%)	UL-94 test (0.8 mm)		
		Average sample burning time (s)	Flaming dripping	UL-94 rating
0:1	36.4	8.4	No	V-0
1:8	33.6	7.1	No	V-0
1:6	33.1	4.7	No	V-0
1:4	32.0	9.6	No	V-0
1:2	26.0	> 50	Yes	No rating

Table 2 present LOI value and UL rating of PP/IFR composites with different loadings of IFR. PP is an easily flammable polymeric material, and its LOI value is only 17.5%. The LOI value of PP/IFR systems dramatically increased with the incorporation of IFR, and when the loading of IFR is 20 wt%, the LOI value could reach 32.4% and the specimens can pass UL-94 V-1 rating with the thickness of 0.8 mm. With the increasing the loading of IFR, the LOI value of PP/IFR composite gradually increased. When the loading of IFR is added to 26 wt%, the slim samples with the thickness of 0.8 mm can successfully pass UL-94 V-0 rating and the LOI value reached 38.0%.

Table 2. LOI and UL-94 data of flame retardant PP composites with different loadings of IFR

Loading of IFR (%)	LOI (%)	UL-94 test (0.8 mm)	
		Flaming dripping	UL-94 rating
0	17.5	Yes	No rating
20	32.4	No	V-1
22	34.9	No	V-1
24	36.4	No	V-1
26	38.0	No	V-0

The LOI value and UL rating of PP/IFR/AHP system with different loadings of AHP/IFR blends are shown in Table 3, and the weight ratio of IFR/AHP is fixed at 6:1. With the increasing of the loading of AHP/IFR, the LOI value of PP/IFR/AHP system gradually increased. When the loading of AHP/IFR is only 24 wt%, the samples with the thickness of 0.8 mm can successfully pass UL-94 V-0 rating. Compared with IFR, the AHP/IFR composite showed higher flame retardant efficiency for PP matrix.

Table 3. LOI and UL-94 data of flame retardant PP composites with different loadings of IFR/AHP

Loading of FR (%) IFR/AHP = 6:1	LOI (%)	UL-94 test (0.8 mm)	
		Flaming dripping	UL-94 rating
20	32.3	No	V-1
22	33.4	No	V-1
24	35.8	No	V-0
26	38.5	No	V-0

Mechanical and Rheology Properties

Table 4 presents the changes of rheology properties, tensile, flexural and notched Izod impact strength of flame retardant PP composites versus weight ratio of IFR to AHP. The loading amount of flame retardant was fixed at 24 wt% based on flame retardant PP system. The rheology properties of all samples were estimated by the torque from the Haake Record. It can be seen that the torque of pure PP is 6.4 Nm, as revealed in Table 4. The torque increases to 6.7 Nm when the loading of IFR is 24 wt%, and the torque almost does not change with the loading of AHP increasing in the flame retardant PP system, indicating that the incorporation of flame retardant (IFR and AHP) into PP matrix can not deteriorate the melt viscosity of PP matrix. Comparing with pure PP, the

mechanical properties decrease with the incorporating of flame retardant and the tensile, flexural and notched Izod impact strengths of flame retardant PP composites decrease by 28.5%, 20.9% and 13.0%, respectively. However, the mechanical properties almost do not change with the loading of AHP increasing in the flame retardant PP system.

Table 4. Mechanical and rheology properties of IFR-PP system with different weight ratios of IFR/AHP

IFR/AHP	Torque (Nm)	Mechanical properties		
		Tensile strength (MPa)	Flexural strength (MPa)	Notched Izod impact ($\text{kJ}\cdot\text{m}^{-2}$)
0:0	6.4	33.3	42.9	4.6
1:0	6.7	23.8	33.9	4.0
2:1	6.6	23.6	34.0	3.9
4:1	6.6	23.5	33.6	4.1
6:1	6.6	23.7	33.4	4.0
8:1	6.7	23.4	33.8	4.1

The effect of IFR/AHP loading on the rheology and mechanical properties of flame retardant PP composites is shown in Table 5, and the weight ratio of AHP to IFR is fixed at 1:6. The torque of pure PP is 6.4 Nm, as revealed in Table 4. The torque is 6.6 Nm when the loading of IFR/AHP is 20 wt%, and the torque is almost not changed with the loading of IFR/AHP increasing in flame retardant PP composites. Compare with the torque of pure PP, the incorporation of IFR/AHP into PP matrix almost does not change the processing properties of PP. The incorporation of IFR/AHP into PP matrix clearly affects the mechanical properties and the mechanical properties of the flame retardant PP system gradually decrease with the increasing of the loading amount of IFR/AHP blends. For example, when the loading of IFR/AHP is 26 wt%, the tensile, flexural and notched Izod impact strengths of flame retardant PP composites decrease by 32.1%, 27.0% and 19.6%, respectively. According to mechanical properties data, it can be deduced that the effect of IFR/AHP blends on mechanical properties of the flame retardant PP system was not obvious.

Table 5. Mechanical and rheology properties of IFR-PP composites with different loadings of IFR/AHP

Loading of IFR/AHP	Torque (Nm)	Mechanical properties		
		Tensile strength (MPa)	Flexural strength (MPa)	Notched Izod impact ($\text{kJ}\cdot\text{m}^{-2}$)
0	6.4	33.3	42.9	4.6
20	6.6	26.1	36.9	4.3
22	6.6	25.5	36.6	4.1
24	6.6	23.7	33.4	4.0
26	6.7	22.6	31.3	3.7

Thermal Degradation Behavior

The IFR, AHP and IFR/AHP systems whose mass ratio is fixed at 6:1, were analyzed by TGA under pure nitrogen atmosphere, and the degradation curves and thermogravimetric analysis data are shown in Fig. 1 and Table 6, respectively. As revealed in Table 6, IFR shows good thermal stability and its initial decomposing temperature is 271 °C based on 1 wt% mass loss. It can be found that the thermal degradation behavior of IFR is classified into three steps, as shown in Fig. 1(a). The peak of step one is at 325 °C, which can be assigned to the releases of the water and ammonia, the second peak appeared at 440 °C, which can be attributed to the decomposition and char-forming of IFR, and the last one appeared at 686 °C, which can be assigned to the decomposition of the char residue^[22]. As shown in Fig. 1(a), the decomposition of AHP is characterized by two steps with two maximal mass loss rates at 340 °C and 430 °C, the first step can be assigned to the decomposition to phosphine and hydrogen phosphate aluminum, and the second one is attributed to the dehydration of aluminum hydro-phosphate to the aluminum polyphosphate^[21]. PH_3 and H_2O are the main decomposition products of AHP at the first and second steps respectively. With the incorporation of AHP in IFR, the initial decomposing temperature of IFR is decreased from 271 °C to 258 °C due to the interaction between AHP and

IFR, that is, AHP may catalyze the esterification reactions between CFA and APP because of the decomposition of AHP and forming phosphine. According to the char residue results revealed in Table 6, the char residue of IFR/AHP complex was 42.6 wt% at 800 °C, which is higher than the calculation result of 37.3 wt% obtained from the calculation based on the mass ratio and the char residue from the experimental result of IFR and AHP at 800 °C, respectively. Therefore, we can draw a conclusion that there are synergistic effect between AHP and IFR, and AHP can improve the char-forming ability for IFR.

Comparing to the DTG curve of IFR, the thermal degradation behavior of IFR/AHP system is different, especially in the range of high temperatures. Similar to IFR, the IFR/AHP system has three peaks and decomposes faster than IFR, as shown in Fig. 1(b). The first mass loss peak of IFR/AHP composite decreased from 325 °C to 300 °C and the intensity is similar to that of IFR, as shown in Table 6, but the intensity of the second and third peaks on DTG curves is dramatically weakened, while these peaks clearly appear in the curve of IFR. This fact illuminated that the incorporation of AHP into IFR, the thermal degradation behavior of IFR changed, where AHP evidently promoted the char formation of IFR/AHP system, and the chemical interaction between AHP and IFR may lead to the formation of char layer with particularly thermal stability at high temperatures, and above 600 °C, the temperature has no effect on its solid residue. A conclusion can be drawn that AHP may stimulate the thermal degradation of IFR at the earlier degradation stage to form a compact char which can delay the further thermal decomposition of IFR at high temperatures.

Table 6. TGA and DTG data of IFR, AHP and IFR/AHP systems under nitrogen

Sample	T_{initial} (°C)	$R_{1\text{peak}}/T_{1\text{peak}}$ (% min ⁻¹ /°C)	$R_{2\text{peak}}/T_{2\text{peak}}$ (% min ⁻¹ /°C)	$R_{3\text{peak}}/T_{3\text{peak}}$ (% min ⁻¹ /°C)	Char residue (%)
					800 °C
IFR	271	-2.0/325	-1.6/440	-2.9/686	30.8
AHP	301	-7.7/340	-1.2/430	—	76.0
IFR/AHP	258	-2.1/300	-1.3/395	-1.1/538	42.6

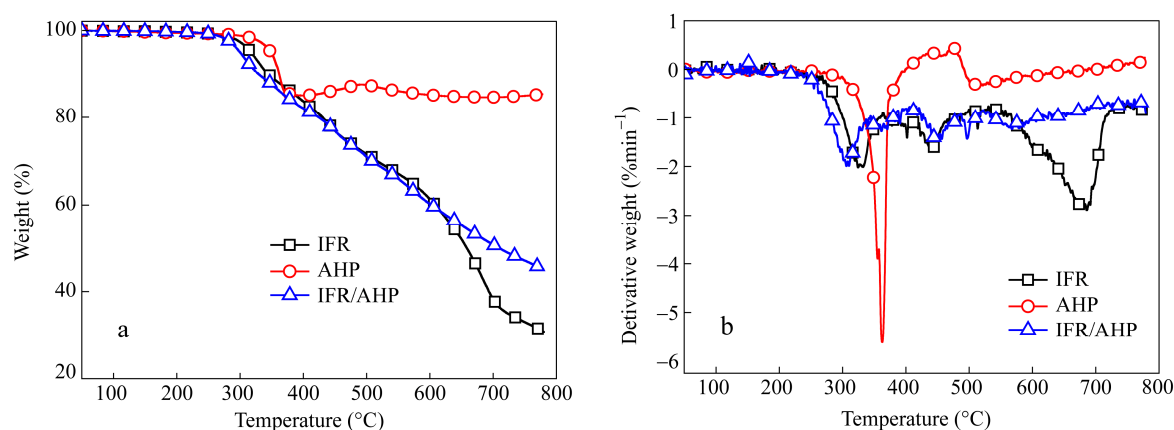


Fig. 1 TGA (a) and DTG (b) curves of IFR, AHP and IFR/AHP blend under nitrogen

The thermal degradation curves for neat PP, PP/IFR, PP/AHP and PP/IFR/AHP composite samples with the total loading of flame retardant was fixed at 24 wt% under pure nitrogen are given in Fig. 2 and the detailed data are listed in Table 7. The neat PP begins to degrade at 254 °C based on 1 wt% mass loss showing one sharp decomposition peak at 354 °C, almost no char residue remained over 500 °C. With the IFR incorporated into PP, the initial decomposition temperature (T_{initial}) and the maximum thermal decomposition temperature (T_{peak}) of PP/IFR enhanced from 254 °C and 354 °C to 264 °C and 385 °C, respectively. It indicates that IFR promote the char formation of PP at high temperatures to form compact char layer, which helps to prevent heat and fuel transfer from the flame zone to the underlying materials, restrained the diffusion of the volatile small molecules into the combustion zone, thus enhances the thermal decomposition temperature. When AHP is introduced to

PP/IFR system, the T_{initial} of PP/IFR/AHP composite is decreased from 264 °C to 214 °C compared with that of the PP/IFR system. It is revealed that AHP change the thermal degradation mechanism and evidently promote PP/IFR to degrade early. The char residue enhanced from 9.5 wt% to 10.7 wt%, which illuminated that AHP could produce phosphoric acid at higher temperatures and the formed phosphoric acid could partly produce the poly-metaphosphoric acid by dehydration, which could promote the carbonization of charring-foaming agent^[19]. However, the T_{peak} of PP/IFR/AHP composite is increased from 385 °C to 427 °C, as revealed in Fig. 2(b), indicating that the more char residue and more compact char layer with higher strength and thermal stability are formed under pyrolysis conditions, which may protect PP from decomposition and prolong the thermal decomposition temperature.

Table 7. TGA and DTG data of neat PP and flame retardant PP systems under nitrogen

Sample	T_{initial} (°C)	$R_{1\text{peak}}/T_{1\text{peak}}$ (% min ⁻¹ /°C)	Char residue (%)
			800 °C
PP	254	-13.1/354	0
PP/IFR	264	-9.2/385	9.5
PP/AHP	261	-8.2/442	19.1
PP/IFR/AHP	214	-8.9/427	10.7

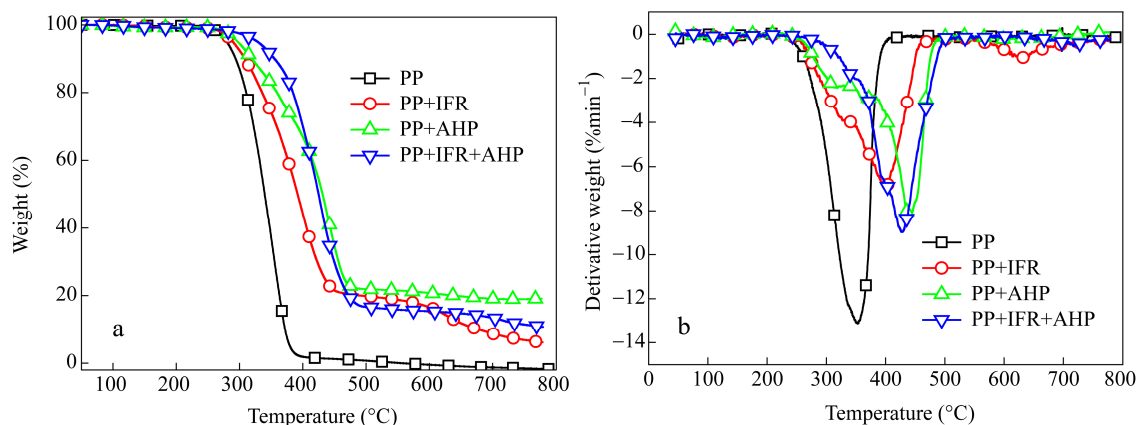


Fig. 2 TGA (a) and DTG (b) curves of PP and flame retardant PP systems under nitrogen

Flammability Behavior

The cone calorimeter (CONE) has been widely used to evaluate the combustion performance of polymeric materials based on the oxygen consumption principle, and the results have good correlation with real fire disaster. The parameters, including time to ignition (TTI), the heat release rate (HRR), the peak heat release rate (PHRR), the total heat release (THR), mass loss rate (MLR), and smoke produce rate (SPR) and total smoke produce (TSP), are determined and used to predict the combustion behavior of materials in real fires^[22]. Figures 3–4 and Table 8 present the plots and the detailed information of combustion behavior for neat PP, PP/IFR, PP/AHP and PP/IFR/AHP systems with the flame retardant loading of 24 wt% obtained from the cone calorimeter test at a heat flux of 50 kW·m⁻².

TTI is used to determine the influence on ignitability, which can be measured from the onset on an HRR curve. TTI showed clear differences in the ignition behavior of the different samples, as shown in Table 8, TTI of PP/IFR system is shorter than that of pure PP, the reason of this phenomenon may be that the surface temperature of the PP/IFR composite rises quickly because the composite decomposes in air and forms phosphoric and polyphosphoric acids which may accelerate the thermal decomposition of the material surface and the char layer formation. TTI of PP/AHP composite is decreased from 34 s for pure PP to 23 s, which indicating that the incorporation of AHP into PP matrix composite shortens the ignition time of materials. The reason is that AHP decomposes at the initial stage of heating and produces the combustible gas of PH₃^[23],

resulting in the easy ignition of PP/AHP composite and the shorter TTI. However, TTI of PP/IFR/AHP composite (IFR/AHP = 6) is prolonged to 33 s and almost similar to that of pure PP because AHP first reacted with IFR at the initial stage of heating as revealed in TGA test.

Figure 3 gives the HRR and THR curves of neat PP, PP/IFR, PP/AHP and PP/IFR/AHP systems. The HRR is recognized to be the most important parameter to quantify the size of fire, and an effective flame retardant system normally shows a lower HRR value. The results revealed that the neat PP resin burns rapidly after ignition and one sharp HRR peak appears with a peak HRR and THR value of $1052.4 \text{ kW}\cdot\text{m}^{-2}$ and $4327 \text{ MJ}\cdot\text{m}^{-2}\cdot\text{kg}^{-1}$, respectively. In contrast, the curves of the PP/IFR and PP/IFR/AHP composites show much lower peaks and longer combusting time, their peak HRR values were decreased remarkably from $1052.4 \text{ kW}\cdot\text{m}^{-2}$ for neat PP to 241.3 and $245.1 \text{ kW}\cdot\text{m}^{-2}$, the THR values decreased significantly from $90.8 \text{ MJ}\cdot\text{m}^{-2}$ to 84.7 and $83.2 \text{ MJ}\cdot\text{m}^{-2}$, respectively, as revealed in Table 8. The HRR curve of PP/IFR composite showed two peaks, however, the second peak of PP/IFR/AHP system was not so clear, as shown in Fig. 3(a). The results may be attributed to that the incorporation of AHP into PP/IFR composite can enhance the strength of intumescent char shield, prevent the char layer from cracking, resist the heat and oxygen transferring into the interior matrix and flammable volatiles into flame zone, which result in suppressing the further degradation of polymer. The decomposition behavior is in agreement with the TGA results discussed above.

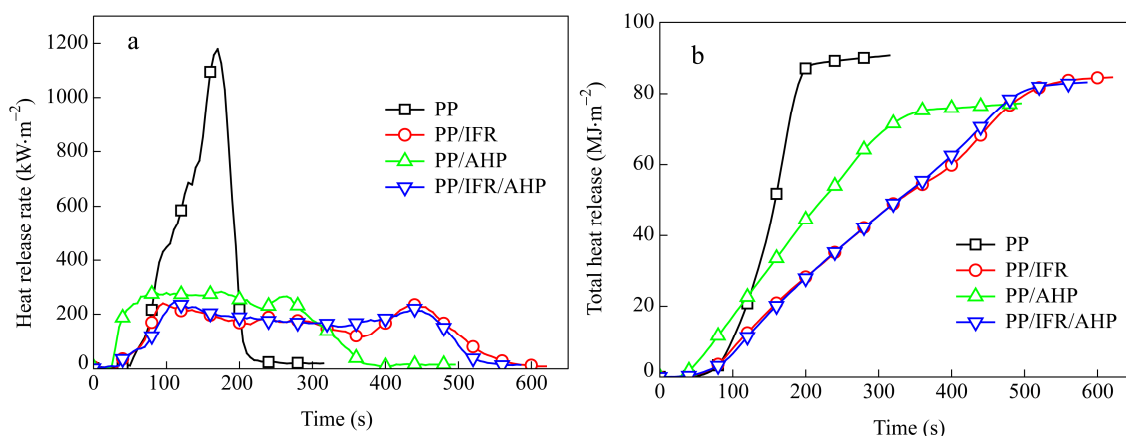


Fig. 3 The HRR (a) and THR (b) curves of neat PP and flame retardant PP systems

Table 8. Cone results of neat PP and flame retardant PP materials

Properties	Sample			
	PP	PP/IFR	PP/AHP	PP/IFR/AHP
TTI (s)	34	30	23	33
peak ₁ -HRR ($\text{kW}\cdot\text{m}^{-2}$)	1052.4	241.3	284.6	245.1
<i>t</i> peak ₁ -HRR (s)	210	95	175	110
peak ₂ -HRR ($\text{kW}\cdot\text{m}^{-2}$)	—	236.6	267.1	221.0
<i>t</i> peak ₂ -HRR (s)	—	440	265	440
THR ($\text{MJ}\cdot\text{m}^{-2}$)	90.8	84.7	77.3	83.2
peak ₁ -SPR ($\text{m}^2\cdot\text{s}^{-1}$)	0.130	0.054	0.096	0.066
<i>t</i> peak ₁ -SPR (s)	200	105	180	105
peak ₂ -SPR ($\text{m}^2\cdot\text{s}^{-1}$)	—	0.058	—	0.053
<i>t</i> peak ₂ -SPR (s)	—	435	—	445
TSP ($\text{m}^2\cdot\text{kg}^{-1}$)	583.5	616.4	819.9	685.1
peak ₁ -COP ($\text{g}\cdot\text{s}^{-1}$)	0.015	0.003	0.013	0.004
<i>t</i> peak ₁ -cop (s)	210	105	190	150
peak ₂ -COP ($\text{g}\cdot\text{s}^{-1}$)	—	0.003	—	0.003
<i>t</i> peak ₂ -cop (s)	—	445	—	455

The smoke production along with the HRR also considered as another critical parameter in fire. The SPR curves of the four samples are presented in Fig. 4. Compared with the SPR curve of neat PP, the value of PP/AHP composite with the AHP loading of 24 wt% appears lower and the peak appears earlier due to the rapid decomposition of AHP on the sample surface at the initial stage of heating, as revealed in Fig. 4. The main decomposition products of AHP are PH_3 and H_2O ^[23], PH_3 can catch the radicals produced from the decomposition of PP resin and inhibit the further degradation of PP, and act the gas phase flame retardant mechanism, resulting in amount of smoke emission. Meanwhile, the SPR curves are similar to the HRR curves and the values of the PP/IFR and PP/IFR/AHP systems are far lower than that of neat PP due to the formation of compact and continuous char layer on the surface of the materials which can inhibit the emission of smoke. The peak of SPR for PP/IFR and PP/IFR/AHP appears earlier than that of neat PP, that is because at the initial stage of heating, the surface temperature of the two samples raises quickly, resulting in the rapid decomposition of IFR and AHP on the surface of the sample. As shown in Fig. 4, the SPR curve of PP/IFR/AHP system is higher than that of PP/IFR composite for the incorporation of AHP into PP/IFR, which increased the amount of smoke emission. The conclusion can be drawn that AHP combined with IFR enhanced the smoke emission of the intumescent flame retardant PP materials.

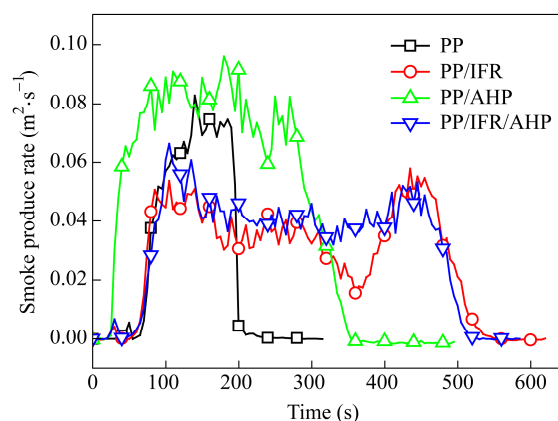


Fig. 4 The SPR curves of neat PP and flame retardant PP systems

Morphologies of the Char Residue

In order to further investigate the relationship between the microstructure of the intumescent char layers and flame retardant properties of flame retardant PP composite, the intumescent char residue of PP/IFR and PP/IFR/AHP composites after cone calorimeter tests was measured by SEM as presented in Fig. 5. We can see that both samples (with or without AHP) produced an intumescent outer surface, and the microstructures of char residue of PP/IFR composite is a relatively loose structure including some small crevasses and holes on the surface (Fig. 5a) due to insufficient char formation during combustion, therefore, heat and flammable volatiles

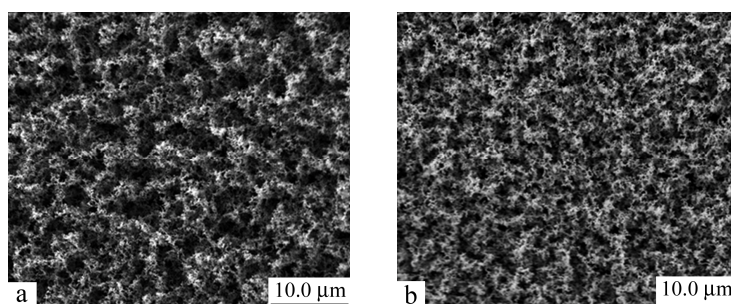


Fig. 5 SEM images of the char residue of flame retardant PP composites: (a) PP/IFR and (b) PP/IFR/AHP

could penetrate the char layer into the flame zone. On the contrary, the char layer for PP/IFR/AHP composite is more homogenous and compact than the former, as revealed in Fig. 5(b). The results suggest that the introduction of AHP into PP/IFR system stimulate to form crosslink network on the char layer surface, resulting in a more compact char layer with better mechanical performance, and consequently the char layer possesses higher thermal stability, which may effectively stop the transfer of heat and flammable volatiles leading to excellent flame retardancy and the high temperature stability of PP/IFR/AHP system.

Chemical Compositions of the Char Residue

XPS is an effective measurement method to study the surface chemical structure of samples without destruction. In order to investigate the relationship between the chemical component of char layer and the flame retardant properties, the chemical composition of the residual char surface of PP/IFR, PP/AHP and PP/IFR/AHP composites after cone calorimeter testing are analyzed by XPS, and the results are listed in Table 9. It is found that the relative content of C of the char residue surface for PP/IFR and PP/AHP composites is 50.9% and 26.7%, respectively. When AHP was incorporated into PP/IFR, the relative contents of C and P are increased from 50.9% and 5.8% for PP/IFR composite to 57.7% and 6.7%, respectively and higher than those of PP/IFR composite. The increasing of the relative content of C and P is aroused by the presence of AHP, indicating that AHP performs a catalytic effect between flame retardant and PP matrix, and promotes the formation of more sufficient char. More flame retardant elements of C and P existing in the formed char layer can enhance the strength of the char layer^[22] resulting in the increasing of thermal stability of PP/IFR/AHP system at high temperatures. Consequently, the flame retardancy of PP matrix is enhanced when the materials are burning.

Table 9. Element relative content of the char layer for flame retardant PP by XPS analysis

Element	Char layer of PP/IFR		Char layer of PP/AHP		Char layer of PP/IFR/AHP	
	Peak BE (eV)	Atomic percentage (%)	Peak BE (eV)	Atomic percentage (%)	Peak BE (eV)	Atomic percentage (%)
C1s	284.2	50.9	284.1	26.7	284.2	57.7
O1s	532.0	29.1	532.1	48.8	531.8	23.5
N1s	398.7	12.5	399.6	1.1	399.4	9.9
Si2p	102.9	0.9	—	—	102.7	0.9
P2p	133.4	5.8	134.3	16.9	133.5	6.7
Al2p	—	—	75.0	6.5	74.4	0.8

CONCLUSIONS

The combination of AHP with IFR based on APP and CFA presented an evident synergistic effect and excellent flame retardant efficiency to PP, the specimen with the thickness of 0.8 mm can pass UL-94 V-0 rating and LOI value reaches 33.5% when the flame retardant loading is 24 wt%, and the optimum mass fraction of AHP/IFR is 1:6 in the flame retardant PP composite. Incorporation of AHP into IFR and PP/IFR obviously promotes the forming of char layer with higher thermal stability. The results of cone calorimeter experiments confirmed that AHP acts as an effective flame retardant synergist. The morphological structure of char residue proves that the addition of AHP into PP/IFR system is benefit to the formation of a more compact and homogeneous char layer on the materials surface during burning, which turns out to be of most important for the flame retardant performance. The analysis of XPS indicates that AHP performs a catalytic effect and promotes the formation of sufficient char on the materials surface and improves the flame retardant properties.

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