Exploring the effect of melamine pyrophosphate and aluminum hypophosphite on flame retardant wood flour/polypropylene composites

Panpan Zhao, Chuigen Guo, Liping Li *

College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China

HIGHLIGHTS

- Incorporation of MPP and AHP into the PP/WF composite significantly improved the thermal stability and char forming ability.
- PHRR and THR of the PP/WF composite reduced remarkably by the addition of MPP/AHP.
- The system of MPP/AHP was equipped with perfect effect of gas phase and condensed phase flame retardancy.

ARTICLE INFO

ABSTRACT

In this examine, melamine pyrophosphate (MPP) and aluminum hypophosphite (AHP) were selected as flame retardants. The synergistic effect between the MPP and AHP on flame retardancy and thermal stability of the polypropylene (PP)/wood flour (WF) composite were investigated. The thermal stability and char forming ability were enhanced considerably for the PP/WF composite with 20 wt% MPP/AHP (3:1), which were indicated by the thermal gravimetric analysis (TG), along with reductions in the heat release rate (HRR) and the smoke production release rate (SPR). The outcomes of TG, scanning electron microscopy and energy-dispersive X-ray spectroscopy revealed that there were inert gases as well as more phosphates and phosphoric acid formed. Which effectively diluted flammable gases and enabled more intumescent char residue to form. In summary, the system of MPP/AHP was equipped with perfect effect of gas phase and condensed phase flame retardancy, endowing PP/WF composite with outstanding capacity of inflaming retarding.

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1. Introduction

Nowadays, wood-plastic composites (WPCs) as potential material had captured both researchers' and manufacturers' attention with excellent characteristics, including recyclability, favorable machinability, low cost, dimensional stability, high stiffness and strength [1–3]. Due to those excellent performances, it had applied to various fields such as furniture, decking, building industries and automobile products etc. [4–6]. However, we cannot ignore the serious limitation caused by high fire risk, which resulted from the two main flammable compositions (natural fibers and thermoplastic plastics) [7–8]. Therefore, it was vital to impart flame retardancy of WPCs, and many efforts had been endeavored in it [9–12].

Intumescent flame retardants (IFRs) have aroused great attention in flame retarded WPCs in recent years, owing to their more environmental-friendly, anti-dripping and lower smoke compared

with the traditional halogen-containing flame retardants [13–15]. Typically, ammonium polyphosphate (APP) was the most effective and widely used IFRs for WPCs, which possessed both acid source and blowing agent, and wood flour (WF) as a charring agent [16–19]. However, the significant disadvantage was that APP can deteriorate the mechanical properties of WPCs due to its hygroscopicity and poor compatibility with organic matrix [2]. One solution to the problem was to employ a new FR possessing acid source and blowing agent such as melamine pyrophosphate (MPP), which had excellent thermostability and water-resistance characteristics widely used to flame retardant nylon [20–22]. However, little work had been done for MPP flame retarded WPCs. Yoshihiko et al. [5] had examined how flame retardants such as ammonium polyphosphate (APP), melamine polyphosphate (MPP) and aluminum hydroxide to impact the flame retardance and mechanical properties of WPCs. It was shared that WPCs with MPP showed the better mechanical properties, but lower flame retardancy than WPCs with APP. Therefore, it was an effective way that seeking a synergistic agent of MPP to overcome this problem. Aluminum hypophosphite

* Corresponding author.
  E-mail address: lilipingguo@126.com (L. Li).

(AHP) has attracted great attention as an efficient environmental friendly and halogen-free flame retardant with the high content of phosphorus [23–25], which may be a good synergistic agent of MPP.

The synergistic effect between MPP and AHP on the PP/WF composite were investigated by limiting oxygen index (LOI), cone calorimetry tests and thermogravimetry analysis (TG). To further study the synergistic mechanism between MPP and AHP, the formation of char layers and their microstructure of WPCs after burning were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX).

2. Experiment

2.1. Materials

Polypropylene (PP) was purchased from Daqing Petro Chemical Company in China with the density of 0.89–0.91 g/cm³ and the melt flow rate of 8 g/10 min (230 °C). Wood flour (WF) was purchased from Harbin Yongxu in China with 80 mesh sieving. Antioxidants–1010 was purchased from Jiangsu Hangguang Company in China. Polypropylene grafted with maleic anhydride (MA-g-PP) was purchased from Hangzhou Haiyi polymer material Ltd. in China. Melamine polyphosphate (MPP) was purchased from Shenzhen Crystal Chemical Co. in China. Aluminum hypophosphite (AHP) was purchased from Qingdao Fu Muslim Chemical Technology Co. in China.

2.2. Sample preparation

The WF was dried at 105 °C for 5–8 h in an electric thermostatic drying oven (DHG-9075A, produced by Shanghai Yiheng Instrument co., Ltd.). PP, AHP and MPP were dried at 60 °C for 4–6 h. Then the dried materials were mixed uniformly in a high speed grinder (FW-80, produced by Tianjin Teste Instrument Co., Ltd.). The samples were prepared by melt blending in the torque rheometer (RM-200, produced by Harbaugh Electric Manufacturing Co., Ltd.) at 180 °C for 8 min, and pressed on a curing machine at 180 °C for 20 s, and then the sheets were formed by high-pressure cooling to test. Table 1 showed the formula of samples. In order to explore the effect of flame retardants on PP/WF composites, the proportion of PP and WF were settled as 2:3.

2.3. Measurements

2.3.1. The limited oxygen index (LOI)

LOI was measured by a JF-3 Oxygen Index Meter (Jiangning Analysis Instrument Company, China) as standard ASTM D-2863. The specimen dimension used was 130 × 6.5 × 3 mm³.

2.3.2. The UL-94 vertical tests

The UL-94 vertical test was measured by a CFZ-3 Vertical Burning Instrument (Jiangning Analysis Instrument Company, China) as standard ASTM D-3801. The dimensions of samples tested were 1 25 × 13 × 3.2 mm³.

2.3.3. Thermogravimetric analysis (TG)

TG was measured using a Pyris 1 Thermal Analyzer (Perkin–Elmer Company, US). Samples were measured under nitrogen at a heating rate of 10 °C/min with a mass of 3–5 mg from 30 °C to 800 °C.

2.3.4. Scanning electron microscopy (SEM)

The morphologies of char residue were observed using a Quanta200 Scanning Electron Microscopy (FEI Company, England). The thickness of specimens was about 2–3 mm, fixed on the sample stage and coated with a conductive layer of gold at the acceleration voltage of 5 kV.

2.3.5. Energy-dispersive X-ray spectroscopy (EDX)

The element content of surface residue was examined by INCA type EDX instrument (the British Oxford Instrument Company). Specimens were coated with a conductive layer of gold.

2.3.6. Cone calorimeter

The cone calorimeter (CONE) tests were executed according to the ASTME 1354-2009 standard. The specimen was wrapped in aluminum foil and placed horizontally with external heat flux of 50 kW·m⁻². The dimension of specimen used was 100 × 100 × 3 mm³.

3. Results and discussion

3.1. LOI and UL-94 vertical tests

The LOI values and UL-94 rating for the samples were summarized in Table 2. According to the results, the sample 1 was flammable in nature with a low LOI value of 23.7 vol%, no UL-94 rating and serious flaming dripping. The LOI values of sample 2 and sample 3 were 27.4 and 26.3 vol% respectively, but they had no UL-94 rating as well.

This indicated that MPP and AHP had little effect on flame retardant PP/WF composite when adding individually. When MPP and AHP were imported simultaneously, the LOI values were higher than that of sample 2 and sample 3. Especially, for sample 6, when the mass ratio of MPP and AHP was 3:1, the LOI value was enhanced by 23.2 vol% with no flaming dripping, and the UL-94 test passed V-0 rating. According to LOI and UL-94 tests, the dual-flame retardant systems showed better flame retardance compared with single-flame retardant systems. Hence, the MPP/AHP (3:1) system demonstrated high efficiency and synergistic effect on PP/WF composite.

Table 1
Components of PP/WF composites.

Samples	PP/wt%	WF/wt%	MA-g-PP/wt%	Antioxidant 1010/wt%	MPP/wt%	AHP/wt%	Ratio (MPP:AHP)
1	36.0	54.0	9.0	1.0	0	0	–
2	28.0	42.0	9.0	1.0	20.0	0	–
3	28.0	42.0	9.0	1.0	0	20.0	–
4	28.0	42.0	9.0	1.0	17.5	2.5	7:1
5	28.0	42.0	9.0	1.0	16.7	3.3	5:1
6	28.0	42.0	9.0	1.0	15.0	5.0	3:1
7	28.0	42.0	9.0	1.0	10.0	10.0	1:1
8	28.0	42.0	9.0	1.0	5.0	15.0	1:3
9	28.0	42.0	9.0	1.0	3.3	16.7	1:5
10	28.0	42.0	9.0	1.0	2.5	17.5	1:7

Table 2
Combustion results of PP/WF composites.

Samples	UL-94	LOI/vol%	Flaming dripping
1	–	23.7	Yes
2	–	27.4	Yes
3	–	26.3	No
4	V-2	27.7	Yes
5	V-1	28.5	No
6	V-0	29.2	No
7	V-1	28.8	No
8	V-2	28.1	No
9	V-2	27.8	No
10	–	27.5	No

3.2. Thermal degradation behavior

The thermogravimetric analysis curve (TG) and the derivative thermogravimetric curve (DTG) curves of samples 1, 2, 3 and 6 are shown in Fig. 1. Correlative data are summarized in Table 3. The DTG of sample 1 exhibited two main mass losses, and that of samples 2, 3 and 6 went through three main mass losses. The first decomposition peak was assigned to the loss of thermal decomposition of MPP and AHP. The second degradation shoulder was attributed to the decomposition of wood flour. And the last peak occurred from the decomposition of PP.

With respect to sample 6, the $T_{5\%}$ was decreased from 280.8 to 277.9 °C, and the T_3 was promoted from 410.2 to 483.6 °C in comparison with sample 1, the T_1 was dropped to 296.3 °C compared with sample 2 (309.3 °C) and sample 3 (314.1 °C). Moreover, the residue char of sample 6 at 800 °C was enhanced from 6.0 to 31.2%, which higher than the calculation result of 25.6% that acquired from the count according to the char residue obtained from experiment and mass ratio of samples 2 and 3 likewise. The decomposition peak of sample 6 diminished in contrast with sample 1, indicated that the decomposition rate was reduced with addition of MPP and AHP. It confirmed that the flame retardants worked effectively during the thermal degradation of matrix by decomposing prior to matrix, since the thermal degradation temperature of flame retardants was lower than that of matrix. In view of this phenomenon, the conceivable flame-retardant mechanism was sketched. The decomposition of MPP took place before matrix attributing to the volatilization of N_2 and NH_3, the vaporized melamine provided an inert gas source, diluting the oxygen and flammable gases present at the point of combustion [26]. Meanwhile, AHP could generate phosphates [23], which were able to raise the char residue via cross-linking with wood, and phosphoric acid

formation then facilitated phosphorylation of cellulose making for dehydration and thus char formation.

Another interesting finding was that sample 3 had a maximum of char residue but with lower flame retardance. It might due to that the char residue resulted from AHP was not enough to protect the matrix from heat flow and oxygen. However, sample 6 could form the impact inflated char residue with perfect protection benefiting from the corporate effect of APP and MPP. This was consistent with the observation from Cone calorimeter and SEM below.

3.3. Cone calorimeter study

The cone calorimeter based on the oxygen consumption principle was widely used to evaluate the combustion properties of materials. The flammability characteristics of samples 1, 2, 3 and 6 are analyzed by cone calorimeter tests, and the average heat release rate (HRR), total heat release (THR), smoke production rate (SPR), total smoke release (TSP), were manifested in Fig. 2 and the characteristic data were presented in Table 4.

According to Table 4, the ignition time (IT) of sample 6 (38 s) is much longer than that of sample 1 (23 s), and the THR of sample 6 within 500 s are decreased by 23.7% compared with sample 1 (128.3 MJ·m^{-2}). As shown in Fig. 2(a), it could be observed that sample 1 burned very fast after ignition with a sharp HRR curve at range of 20–50 s. The peaks of heat release rate (PHRR) for samples 1, 2 and 3 present to rates of heat release of 507.2, 347.5 and 347.3 kW·m^{-2}, in the case of sample 6 is reduced to 287.8 kW·m^{-2}. Moreover, the combustion of sample 6 was prolonged to 500 s from 200 s of the control sample 1. The slope of THR curves from Fig. 2(b) could be supposed to the representative of flame spread. It was noteworthy that the flame spread of samples 2, 3 and 6 had decreased, and that of sample 6 was comparatively the lowest. Fig. 2(c) described the smoke production rate (SPR) curves. It revealed that the maximum value of the smoke production rate for sample 6 was obviously smaller than that of sample 1, the similar outcomes could be demonstrated by the TSP curves in Fig. 2(d).

By analyzing the TG, Cone as well as others previous studies, the synergistic mechanism of this flame retardant system was further affirmed. During combustion, MPP and AHP played an essential role in gas phase and condensed phase. AHP could generate abundant phosphates and polyphosphoric acid which enhanced the formation of char layers. In addition, MPP could produce inert gases that diluted flammable gases and spurred the char layer to inflation, thus MPP and AHP acted as an admirable flame retardant synergetic system, leading to a lower PHRR value and longer ignition time. In addition, the formative intumescent char layer could effi-
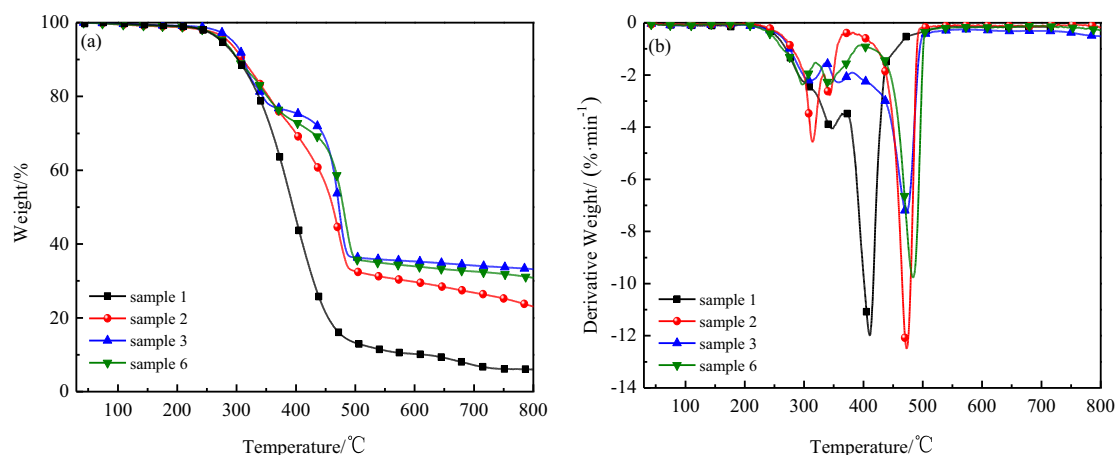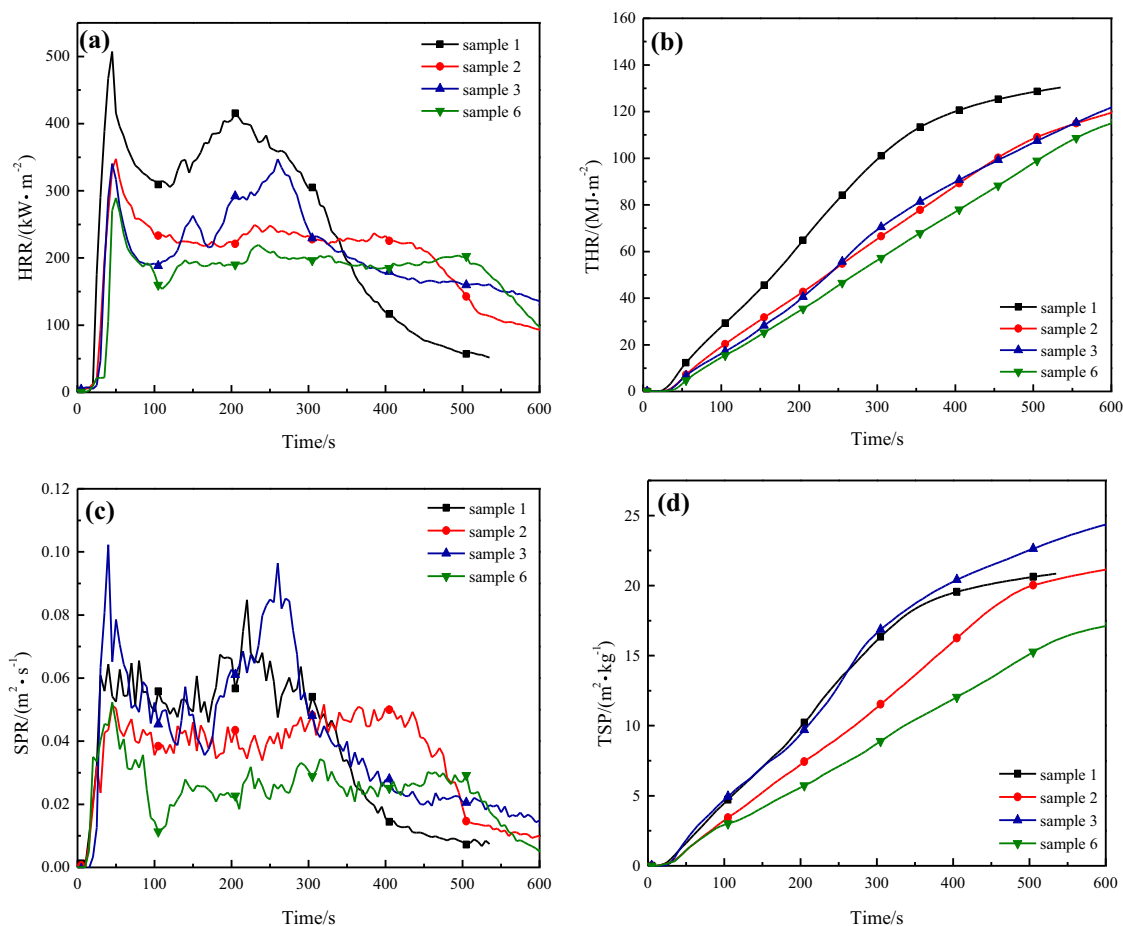

Fig. 1. TG (a) and DTG (b) curves of PP/WF composites.

Table 3
TG and DTG data obtained for PP/WF composites.

Samples	$T_{5\%}$/°C	T_1/°C	T_2/°C	T_3/°C Char residue (800 °C)/%
1	280.8	–	347.4	410.2	6.0
2	286.2	309.3	356.8	470.6	23.1
3	293.7	314.1	342.7	473.0	33.2
6	277.9	296.3	341.9	483.6	31.2

$T_{5\%}$: the temperature at 5% weight loss, T_1: the first peak temperature, T_2: the second peak temperature, T_3: the third peak temperature.

Fig. 2. HRR (a), THR (b), SPR (c), TSP (d) curves of PP/WF composites.

Table 4
Cone calorimeter test data of WF/PP composites.

Samples	IT (s)	PHRR (kW·m^{-2})	THR (MJ·m^{-2})	TSP (m^2·kg^{-1})
1	23	507.2	128.3	20.7
2	32	347.5	108.3	20.0
3	33	347.3	106.6	22.5
6	38	287.8	97.9	15.1

ciently prevent the heat and gas transfer between the fire zone and the burning matrix greatly, thus limited the smoke produce of PP/WF composites.

3.4. Morphological characterization

Fig. 3 shows digital photos of PP/WF composites after cone calorimeter tests. As revealed in Fig. 3(a), it could be easily observed that sample 1 left a little white cottony residue purely. For sample 2, the residue exhibited a discontinuous char layer with a small quantity of residues left in the tray [Fig. 3(b)], which illustrated that MPP had no obviously effect on promoting the formation of char layer and mainly played a role in the gas phase flame retardancy during burning. As shown in Fig. 3(c), a certain amount of char residue kept on the tray with no inflation, which indicated that AHP merely acted as the condensed phase flame retardant for PP/WF composite during combustion. As shown in Fig. 3(d), it found that the char residue showed a two-layer structure with the glossy compact surface layer and intumescent bottom layer, and the sufficient char layer appeared on the tray. It
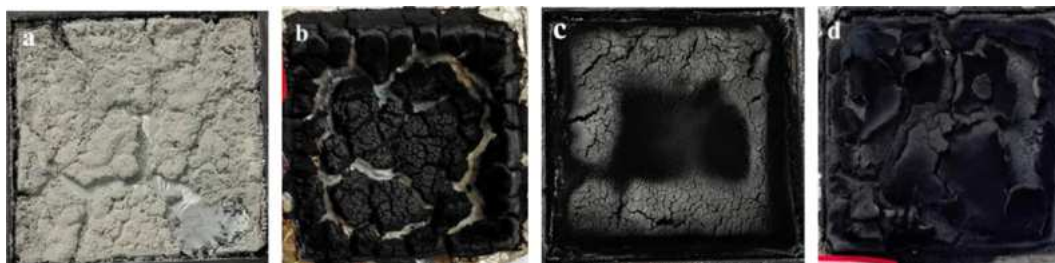
Fig. 3. Digital photos of char formation for PP/WF composites after cone calorimeter, (a) sample 1; (b) sample 2; (c) sample 3, (d) sample 6.

may be attributed to that the incorporation of MPP and AHP stimulated the char layer to inflate due to the gases formation, such as N_2 and NH_3 released by the decomposition of MPP [22]. The vaporized melamine also could dilute the flammable gases and oxygen present at the point of burning, acting as gas phase flame retardancy. Therefore, the flame retardance was enhanced during burning. The foamed char reduced the thermal conductivity at the material interior, as well as the liberative inert gases limited the combustible gases to combust at the material surface, then enhanced the flame retardancy of PP/WF composite, which was in accord with above analysis results.

In order to further explore the microstructure of intumescent char layer, the morphology of the char layers after cone calorimeter tests was measured by SEM. As revealed in Fig. 4(a), the char of sample 1 seems fragile and easy to collapse with crevasses and holes existed on the surface, which was due to insufficient or less condensed char formation during decomposition. When MPP was added alone, it appeared an inhomogeneous, relatively disordered structure with many flaws on the surface for the char layer of sample 2 [Fig. 4(b)], thus this char could not primely prevent heat and

flammable gases from penetrating into the flame zone. From Fig. 4 (c), the sample 3 presented a tighter and thicker char layer compared with sample 2, however it also could not effectively protect the composite from combustion owing to the existence of holes. While the char layer of sample 6 was compact, uniform and tight [Fig. 4(d)], creating an excellent physical barrier to stop the transfer of flammable gases and heat during decomposition, hence the flame retardancy of the composite was enhanced immensely.

3.5. Chemical compositions of the char residue

In order to probe into the relationship between the flame retardancy and the chemical compositions of residual char layer, the surface char residues after cone calorimeter testing were detected by EDX, and the results were presented in Fig. 5. As can be seen form Fig. 5(a)–(d), the relative weight percent of C element for sample 6 on the char surface was 39.43 wt%, much lower than that for samples 1, 2 and 3. However, the relative element contents of O, Al and P were 40.13, 4.42 and 16.02 wt% respectively for sample 6, much higher than that for others. It was apparent that the decom-
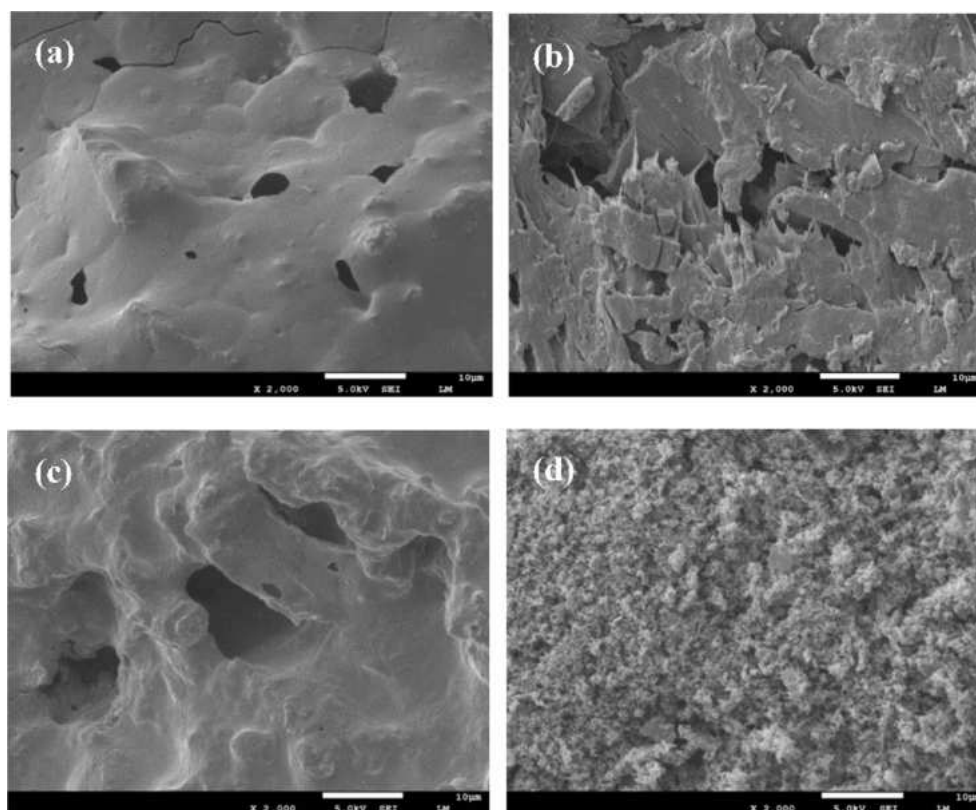

Fig. 4. SEM micrographs of the surface char layer from PP/WF composites after cone calorimeter test. (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 6.
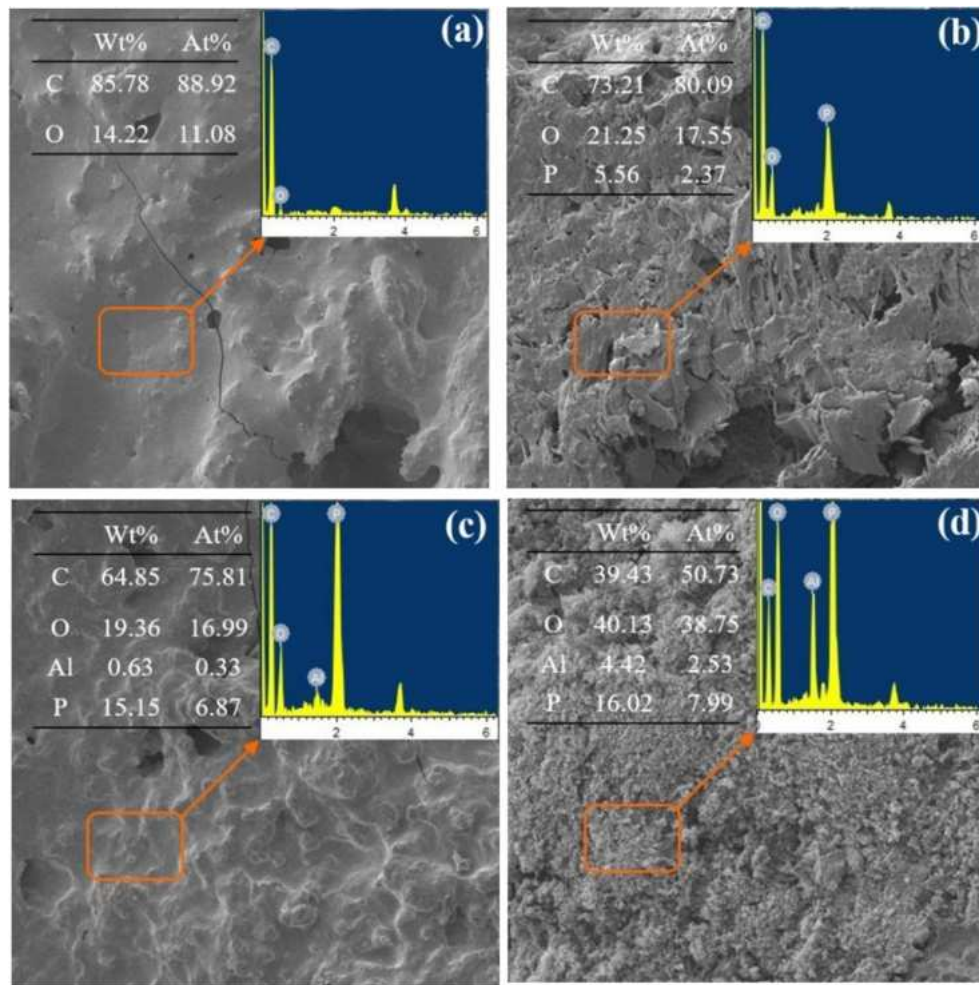
Fig. 5. EDX results of char residues for PP/WF composites. (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 6.

position of sample 6 could produce more phosphates and phosphoric acid given that the more O, Al and P remained, thereby leading to a more cross-linking thermostable char formation during the combustion processes. At last, the less material was consumed attributed to the excellent protect of char residue, so that the external char layer possessed fewer C.

4. Conclusions

The effective use of MPP and AHP for PP/WF composite was evaluated. Regarding to above research, the decomposition of MPP could generate inert gases which reacted on gas phase flame retardancy. Simultaneously, AHP could form more phosphates and phosphoric acid promoting the char residue to take shape, which acted on condensed phase flame retardancy. As a consequence, the LOI value reached 29.2 vol% and UL-94 V-0 rating was obtained when 20 wt% MPP/AHP (3:1) loaded. In addition, PHRR and THR of the PP/WF composite reduced remarkably compared with pure PP/WF composite, decreased by 40.0% and 23.7% respectively by the cone tests. Thus, the combination of MPP and AHP had been proved to be a promising IFR system for PP/WF composite.

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