Effect of Pentaerythritol on the Properties of Wood-Flour/Polypropylene/Ammonium Polyphosphate Composite System

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Intumescent, flame-retarding wood-flour/polypropylene composites (WPCs) having different ammonium polyphosphate/pentaerythritol (APP/PER) ratios (4/1, 3/1, and 2/1) were prepared in this study. The thermal degradation behavior, flame retardancy, and mechanical properties of the composites were tested. Moreover, the residues of the WPCs were observed by scanning electron microscopy, and the flame retardancy mechanism was investigated. The results showed that WPC/APP/PER exhibited higher thermal stability in the high temperature region and left much more char residue than WPC/APP, according to thermogravimetric analysis. Limiting oxygen index and cone calorimetry tests showed that the addition of PER improved the flame retardancy of the WPCs, especially when APP/PER ratio was 3/1. However, because of the poor compatibility with the composite matrix and uneven dispersion in the WPCs, the incorporation of PER decreased the mechanical performance of WPCs obviously.

Keywords: Pentaerythritol; Wood-plastic composite; Intumescent flame retardant; Thermal degradation behavior; Flame retardant mechanism

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INTRODUCTION

Due to environmental concerns and dwindling petroleum resources, wood-plastic composites (WPCs) have drawn more and more attention in the past two decades (García *et al*. 2009). Because of their excellent performance, low cost, high dimensional stability throughout their lifetime, and high relative strength and stiffness (Stark *et al*. 2010; Li *et al*. 2014), WPCs have been widely used in decking products, automotive parts, and construction products (Ashori 2008; Ndiaye *et al*. 2008; Leu *et al*. 2012; Arao *et al*. 2014; Turke *et al*. 2014; Wu *et al*. 2014). However, the main drawback limiting wider application of WPCs is their high flammability, which is because the two main components (wood-flour or fiber and plastic) are themselves flammable (Li *et al*. 2010; Arao *et al*. 2014; Pan *et al*. 2014). Thus, the development of flame-retarding WPCs is of great importance.

The most effective, expeditious method to enhance the flame retardancy of WPCs is to treat them with flame retardants (FRs), among which intumescent flame retardants (IFRs) have been considered promising and are widely used because of their halogen-free nature, low smoke generation, low toxicity, and high efficiency (Bourbigot *et al*. 2004; Demir *et al*. 2005; Arao *et al*. 2014; Bai *et al*. 2014).

The most typical, effective IFR system is the combination of ammonium polyphosphate (APP) and pentaerythritol (PER), in which APP acts as both the acid source and the blowing agent and PER is the char forming agent. These additives play an important role in forming a carbonaceous char. The reaction process of the IFR system was extensively studied in 1980s and 1990s by Bourbigot *et al.* (1993, 1995) and Camino *et al*. (1984a,b,c,d; 1985a,b). Most of the investigations focused on the IFR system in polyolefins (Camino *et al*. 1984a,b,c,d; 1985a,b; Delobel *et al*. 1993; Bourbigot *et al*. 2004; Xia *et al*. 2014), and the optimal APP/PER ratio (weight ratio of APP-to-PER) for the flame retardancy of the polymer matrix was proposed in several studies. However, few studies have focused on the typical IFR system present in WPCs and the corresponding flame retardancy mechanism.

In this work, IFR systems with different APP/PER ratios (4/1, 3/1, and 2/1) were used for the flame retardancy modification of wood-flour/polypropylene composites. The effect of PER on the thermal degradation behavior of the flame-retarding WPCs was investigated by thermogravimetric analysis (TGA). The flame retardancy of the WPCs was evaluated by limiting oxygen index (LOI) and cone calorimetry tests. The surface residues of the WPCs at the end of the cone calorimetry tests were investigated by scanning electron microscopy (SEM) and the corresponding flame retardant mechanism was speculated. In addition, the effect of PER on the mechanical properties of the flame-retarding WPCs was also investigated.

EXPERIMENTAL

Materials

The materials were all made in China. Poplar wood flour (*Populus tomentasa* Carr., particle sizes between 60- and 80-mesh) was kindly provided by Gaocheng Xingda Wood Flour Company. PP (K8303, copolymer, melting point 165 °C, melt-flow rate 1.5 g/10 min) was obtained from Beijing Yanshan Petrochemical Co. APP (average polymerization degree $n > 1000$) was obtained from Shenzhen Jingcai Chemical Co.. PER (chemically pure) was obtained from Shanghai Sinopharm Chemical Reagent Co.

Methods

Preparation of WPCs

The wood-flour was oven-dried at 105 °C until its weight was stable. Then, APP and PER were added into PP and wood-flour (PP/wood-flour ratio of 6/4) at constant weight percentages (Table 1). Each group of raw materials was mixed in a high-speed mixer at a mixing speed of 2900 rpm for 4 min followed by melt-blending in a co-rotating twin-screw extruder (KESUN KS-20, Kunshan, China). The corresponding temperatures in the extruder barrel were controlled to 165, 170, 175, 180, and 175 °C from the hopper to the die zones, respectively, and the screw speed was 167 rpm. Then, the extrudates were cut into small particles about 5 mm in size and dried again at 105 °C for 3 h before being removed for hand matting. A hot press (SYSMEN-ll, China Academy of Forestry, Beijing, China) was used to produce WPCs by compressing the mat under 4 MPa pressure at 180 °C for 6 min. After hot pressing, the mat formed was cooled under 4 MPa pressure at room temperature for another 6 min in a cold press. The control WPC (WPC-0), without IFR, was prepared similarly. The dimensions of the WPCs were 270 × 270 × 3 mm^3 with a target density of 1.0 g/cm^3.

Table 1. Formulation of WPCs

Sample	PP (wt. %)	WF (wt. %)	APP (wt. %)	PER (wt. %)	APP/PE ratios
WPC-0	60	40	0	0	-
WPC-1	42	28	30	0	-
WPC-2	42	28	24	6	4/1
WPC-3	42	28	22.5	7.5	3/1
WPC-4	42	28	20	10	2/1

Analytical tests

All TGA curves were recorded using a Q50 TGA analyzer (TA Instruments, USA) at a linear heating rate of 10 °C/min under a pure nitrogen atmosphere. The temperature ranged from ambient to 600 °C. Each sample was kept within 5 to 8 mg in an open platinum pan.

The LOIs of the all WPCs were measured using an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) with the sheets (135 × 6.5 × 3 mm^3) according to ASTM D2863-77. Fifteen replicates were tested for each group.

Combustion experiments were conducted with a cone calorimeter (Stanton Redcroft, UK) in accordance with ISO 5660 procedures. Each specimen (100 × 100 × 3 mm^3) was wrapped in aluminum foil and exposed horizontally to 35 kW/m^2 external heat flux. Three replicates were tested for each group.

The morphologies of the WPC combustion residues were investigated by a Hitachi S-3400 SEM analyzer (Philips, Japan) with an acceleration voltage of 5 kV.

Mechanical property tests

The flexural properties, including the flexural strength (MOR) and flexural elasticity (MOE), were measured as specified by Chinese standard GB/T 9341-2008, which involves a three-point bending test at a crosshead speed of 5 mm/min. Six replicates (60 × 25 × 3 mm^3) from each group were tested and the standard deviations (SDs) were calculated.

The tensile properties, including the tensile strength and elongation at break, were measured according to Chinese standard GB/T 1040.2-2006 at a testing speed of 2 mm/min. Six replicates (75 × 13 × 3 mm^3) from each group were tested and the SDs were calculated.

Unnotched Izod impact tests were performed in accordance with Chinese standard GB/T 1843-2008. Six unnotched replicates (80 × 10 × 3 mm^3) from each group were tested to calculate the Izod impact strength.

RESULTS AND DISCUSSION

Thermal Degradation Analysis

The TGA and derivative thermogravimetry (DTG) curves of the WPCs are shown in Figs. 1a and b, respectively, and the related DTG data are listed in Table 2. The thermal degradation of WPC-0 and WPC-1 was composed of two steps. The T_{max1} of WPC-1 was lower than that of WPC-0, while T_{max2} was higher (Table 2), indicating that the incorporation of APP significantly accelerated the decomposition of the WPCs, which was consistent with the findings of a previous study (Delobel *et al*. 1993). When WPCs were incorporated with PER, they exhibited three decomposition steps, as shown in Fig. 1

(WPC-2, WPC-3, and WPC-4). The first decomposition step (from about 200 to 250 °C) was attributed to a series of possible esterification reactions (Fig. 2) between APP and PER (Xia *et al*. 2014). With more PER incorporation, WPCs exhibited slightly lower T_{max1}, which could be attributed to the comparatively lower decomposition temperature of PER (about 200 °C) (Camino *et al*. 1984a; Wang *et al*. 2009). Therefore, the more PER added to the WPCs, the comparatively lower the T_{max1} was. The second step (from 250 to 350 °C) represented the decomposition of part of the PP and APP, hemicellulose (225 to 325 °C), and cellulose (325 to 375 °C) in the wood-flour, and further esterification reactions between APP and PER (Arao *et al*. 2014). The carbonaceous foam, a phosphate-carbon mixture containing both soluble phosphorous moieties and insoluble C-rich chars, formed during these two decomposition steps (Vandersall 1971; Camino *et al*. 1984a,b). The soluble phosphorous moieties were phosphorous degradation products from the APP-PER system, which could be defined as PDPs. This carbonaceous foam, with a mixture of rich chars and PDPs, could effectively protect underlying materials from further thermal degradation. Thus, the flame-retarding WPCs containing PER decomposed more slowly and exhibited higher thermal stability than WPC/APP in the last decomposition step and left much more char residue (about 45%) at 600 °C, especially in WPC-3 (47.2%).

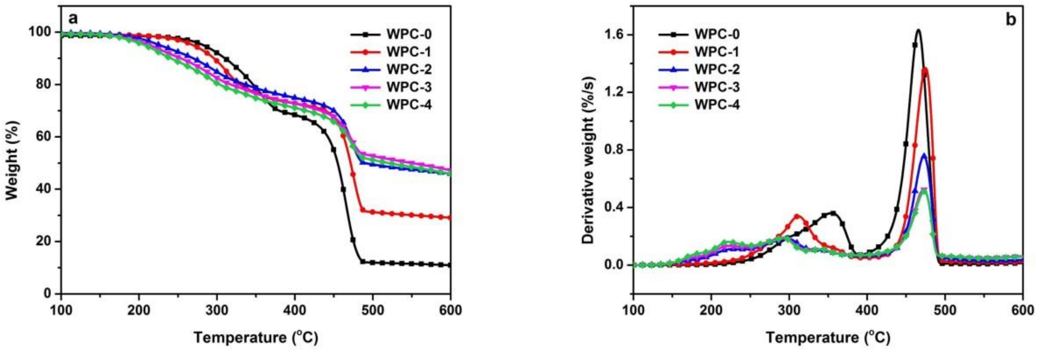

Fig. 1. TGA (a) and DTG (b) curves of WPCs

Table 2. TGA Data of WPCs

	T_{max1} [a]	ML_1 [b]	T_{max2} [a]	ML_2 [b]	T_{max3} [a]	ML_3 [b]	CR[c]
Sample	(°C)	(%)	(°C)	(%)	(°C)	(%)	600 °C (%)
WPC-0	353.8	22.9	465.7	65.8	–	–	11.0
WPC-1	311.9	14.8	474.2	54.7	–	–	29.1
WPC-2	225.1	4.8	297.3	14.6	472.6	41.6	45.9
WPC-3	223.3	6.1	294.1	16.4	472.4	40.9	47.2
WPC-4	222.1	6.9	292.4	18.0	473.2	42.7	45.9

[a] The temperature at which the maximum mass loss occurred during the first, second, and third decomposition step, respectively.

[b] Mass loss for the first, second, and third decomposition step, respectively.

[c] Char residue.

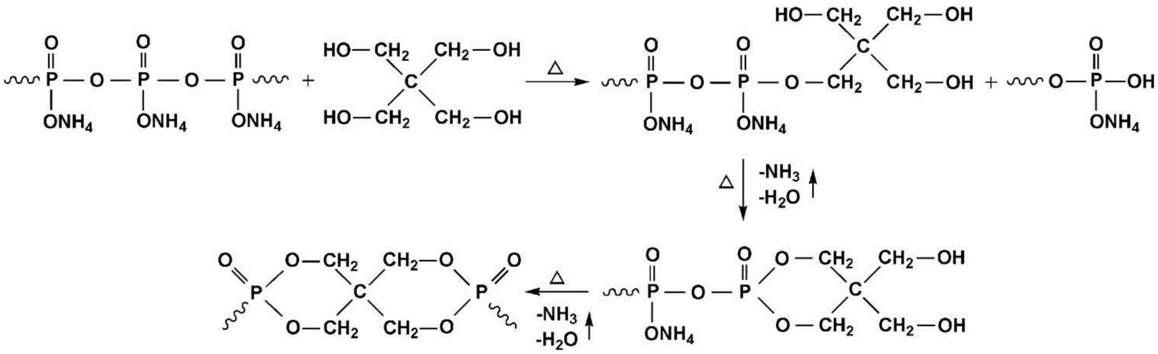

Fig. 2. Possible esterification reactions between APP and PER

Fire Performance of WPCs

LOI tests

LOI tests were used to evaluate the flame retardancy of WPCs, and the results are shown in Table 3. As can be seen, the incorporation of APP increased the LOI value of the WPCs by 17.6% from 20.4 (WPC-0) to 24.0 (WPC-1), indicating that APP imparted the WPCs with better flame retardancy. With further addition of PER, the LOI value of the WPCs was increased by 5.4% (WPC-2) and 6.3% (WPC-3), as compared with WPC-1 (24.0). However, with more PER added to the composites, the LOI value of WPC-4 (25.2) was decreased slightly. It is well known that PER acts as the char forming agent in the IFR system, so the amount of char formed could increase with increasing PER incorporation, thus enhancing the efficiency of heat insulation and increasing the LOI value. However, the results of the LOI tests suggest that there should exist an optimal acid source (or blowing agent)/char forming agent ratio (APP/PER ratio) suitable to effectively achieve the synergistic effect of elemental P/C/N and produce carbonaceous foaming char with a certain hole size (Xia *et al*. 2014). Therefore, 3/1 (WPC-3) could be the optimal APP/PER ratio for the flame retardancy of WPCs.

Table 3. LOI data of WPCs

Sample	WPC-0	WPC-1	WPC-2	WPC-3	WPC-4
LOI (%)	20.4 ± 0.02	24.0 ± 0.03	25.3 ± 0.02	25.5 ± 0.01	25.2 ± 0.02

Cone calorimetry tests

Cone calorimetry can well simulate the behavior of a material in a real fire and was used to further interpret the results of the LOI tests. The ignition time (IT), peak-heat release rate (Pk-HRR), average-heat release rate (Av-HRR), average mass loss rate (Av-MLR), total heat release (THR), average specific extinction area (Av-SEA), and residue weight at the end of the tests are the main parameters to evaluate the combustion behavior of materials. They are summarized in Table 4. The HRR is one of the most significant parameters for flame retardancy evaluation, which is shown in Fig. 3. As can be seen, the composite without flame retardants (WPC-0) burned quickly after ignition and its Pk-HRR was 757.92 kW/m^2. However, other composites exhibited dramatically lower HRR peaks. The THR value of WPC-1 (77.13 MJ/m^2) was slightly lower than those of WPC-2, WPC-3, and WPC-4, which may be because that the actual amount of APP in composites played the important role in decreasing the THR, and WPC-1 contained more APP (30 wt. %) than the other WPCs (Tang *et al*. 2013). Comparatively, HRR, MLR, and SEA data showed the corresponding trends with the LOI data (Table 3). WPC-3 exhibited the lowest HRR, MLR, SEA values, demonstrating that WPC-3 displayed better flame retardancy than the other flame-retarding WPCs. In addition, WPC-2, WPC-3, and WPC-4 yielded much higher residue weights at the end of the test compared with WPC-1, illustrating that PER indeed acted as a char forming agent and promoted the formation of char residues in a real fire.

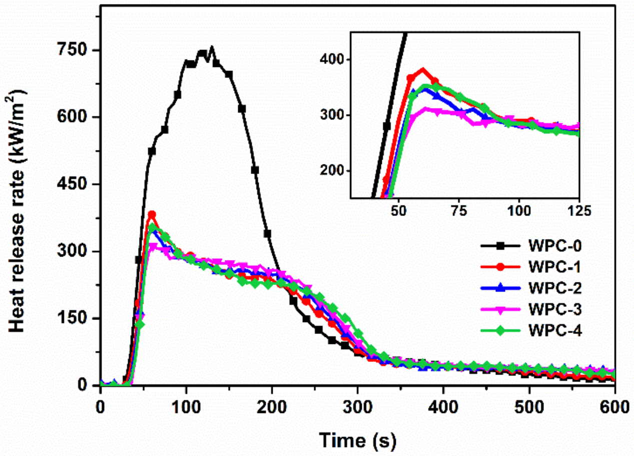

Fig. 3. HRR curves *versus* burning time of WPCs

Table 4. Cone Calorimetry Data of WPCs

	IT	Pk-HRR	Av-HRR	Av-MLR	THR	Av-SEA	Residue Weight
Sample	(s)	(kW/m²)	(kW/m²)	(g/s)	(MJ/m²)	(m²/kg)	(wt. %)
WPC-0	15±1	757.92±3.71	182.27±1.25	0.039±0.001	123.01±1.12	388.67±7.19	7.16±0.73
WPC-1	17±1	382.59±4.25	116.83±1.07	0.034±0.001	77.13±0.47	607.38±7.24	19.82±1.28
WPC-2	19±1	347.21±2.93	109.34±1.25	0.031±0.001	79.03±0.39	543.19±7.03	26.12±1.54
WPC-3	20±1	311.61±4.51	104.12±2.32	0.029±0.001	79.50±0.75	492.17±5.17	28.20±1.31
WPC-4	20±1	353.54±3.67	108.89±1.37	0.032±0.001	81.23±0.58	557.34±6.41	24.79±1.11

Flame Retardant Mechanism

Figure 4 shows the SEM morphology of the surface residues of the flame-retarding WPCs at the end of the cone calorimetry tests. The surfaces of all the residues were covered by an expanded char network. The char residue of WPC-1 contained a large number of channels or gaps which could allow combustible gases and melting polymer to overflow, resulting in further combustion (Wang *et al*. 2015). Compared with that of WPC-1, the chars of WPC-2 and WPC-3 were swollen and there were some successive and randomly scattered bubbles that resulted from the decomposition of APP and the release of volatile gases, including NH_3 and H_2O. These gases could decrease the concentration of O_2 on the surface of the burning materials, playing a positive role in the gas-phase flame retardant mechanism (Fig. 5a). On the other hand, the incorporation of PER promoted the formation of a honeycomb-like, intumescent char, which could prevent the transfer of heat and O_2 between the surface of the burning materials and the underlying matrix, thus decreasing further pyrolysis reactions and improving the flame retardancy of the WPCs (Camino *et al*. 1984a; Wu *et al*. 2008) (Fig. 5b). Therefore, PER had a positive effect on the condensed-phase flame retardant mechanism. However, WPC-4 performed some discontinuous or broken intumescent char network, which may not prevent the transfer of the heat and O_2. These morphologies could further demonstrate the lower flame-retardancy of WPC-4 than that of WPC-2 and WPC-3, which corresponded with the results of LOI and cone calorimetry tests.

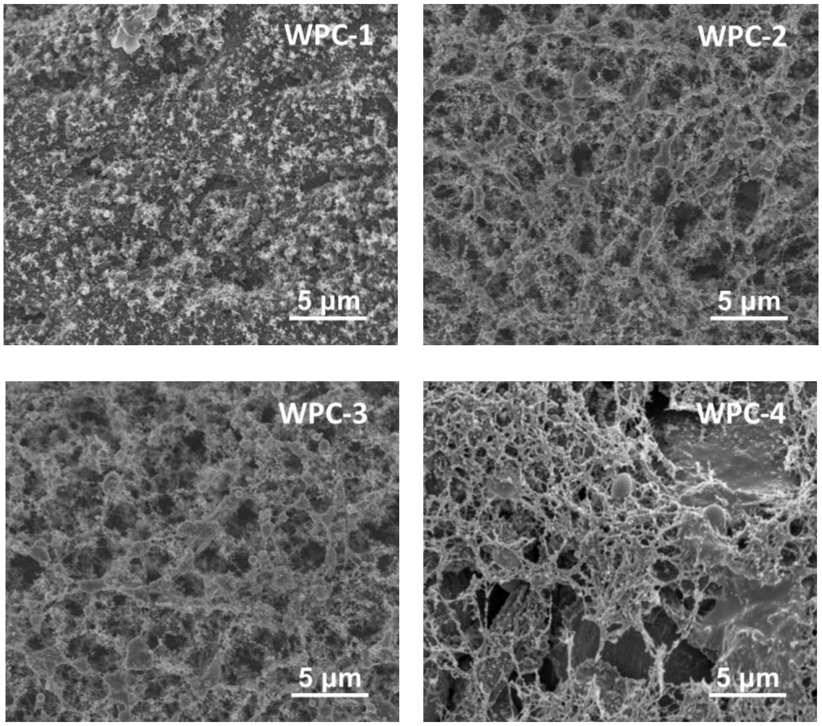

Fig. 4. SEM images of the surface formation char of WPCs

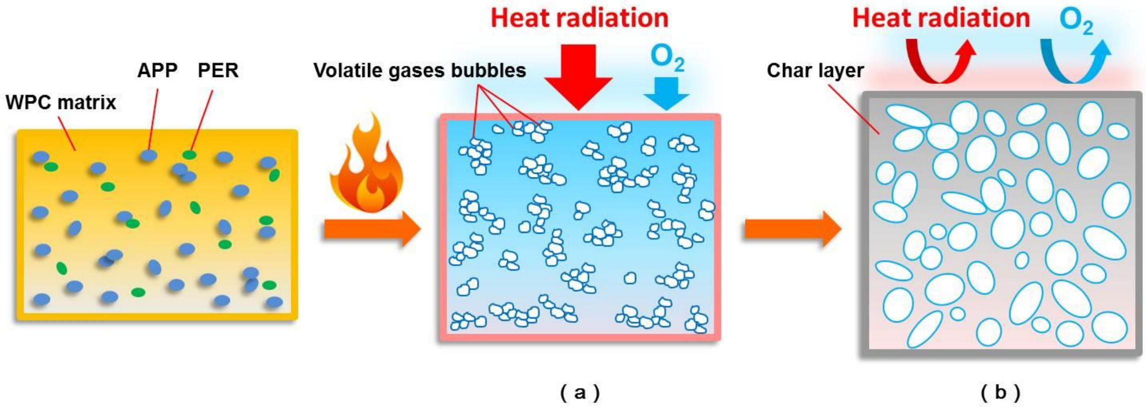

Fig. 5. Possible intumescent flame-retarding process in WPC/APP/PER system

Mechanical Performance of WPCs

The mechanical performance, including the tensile properties, flexural properties, and impact strength of the WPCs, is shown in Table 5. The data presented are the average of six replicates. It was obvious that both the tensile properties and the impact strength of the WPCs decreased with the addition of APP, which was consistent with the findings of the previous reports (Canimo *et al*. 1984a; Ayrilmis *et al*. 2012; Wang *et al*. 2014). In addition, the MOR also decreased with the addition of APP into the WPCs, while the MOE increased. This was because APP had poor compatibility with the WPC matrix, but they could act as rigid particles in the matrix and enhance the MOE of the WPCs to some extent. WPC-1 contained more APP (30 wt. %) than the other flame-retarding WPCs, as a result, it performed the highest MOE value. When PER was incorporated, the mechanical performance of the WPCs decreased as compared with WPC-1, and further decreased with the increment PER in the WPCs. This may be due to the fact that PER had poor compatibility with PP because of their different polarities. On the other hand, the comparatively larger PER particles, with uneven dispersion, had a negative effect on the interfacial bonding between the matrix materials and acted as a site of stress concentration (Mareri *et al*. 1998), reducing the mechanical properties of the WPCs.

Table 5. Mechanical Properties of the WPCs

Sample	Tensile strength	Elongation at break	MOR	MOE	Impact strength
	(MPa)	(%)	(MPa)	(GPa)	(KJ/m^2)
WPC-0	19.00 ± 0.46	2.94 ± 0.14	51.04 ± 1.90	3.17 ± 0.13	4.66 ± 0.02
WPC-1	17.67 ± 0.39	1.68 ± 0.13	45.33 ± 0.73	3.82 ± 0.05	2.83 ± 0.06
WPC-2	15.77 ± 0.35	1.46 ± 0.13	36.75 ± 0.56	3.56 ± 0.03	2.37 ± 0.07
WPC-3	15.16 ± 0.12	1.23 ± 0.12	35.85 ± 0.34	3.51 ± 0.05	2.37 ± 0.08
WPC-4	15.17 ± 0.30	1.06 ± 0.09	35.76 ± 0.79	3.20 ± 0.06	2.36 ± 0.07

CONCLUSIONS

1. Composites containing both APP and PER exhibited higher LOI values and lower HRRs, and left more char residues after combustion than the composites only containing APP (WPC-1), especially WPC-3 with an APP/PER ratio of 3/1, which left 42.3% more residues than WPC-1.
2. The incorporation of PER improved the flame retardancy of WPCs, especially WPC-3 according to the LOI and cone calorimetry tests.
3. The SEM morphologies of the residues from the WPCs indicated that PER promoted the formation of a honeycomb-like intumescent char and had a positive effect on the condensed-phase flame retardant mechanism.
4. The addition of PER decreased the mechanical performance of the flame-retarding WPCs. Therefore, to extend the application of PER, further studies should be focused on improving the interfacial compatibility between PER and the composite matrix.

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