

## THE SYNERGISTIC SMOKE SUPPRESSION EFFECT OF FERRIC OXIDE ON FLAME RETARDANT WOOD-POLYURETHANE COMPOSITES

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(RECEIVED JULY 2017)

### ABSTRACT

Wood flour-polyurethane composites (WPC) with ammonium polyphosphate (APP) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ) were prepared to research the cooperative influence of smoke suppression and fire resistance. By the methods of cone calorimeter test (CCT), smoke density test (SDT), thermogravimetric analysis (TG), limiting oxygen index (LOI), field emission scanning electron microscope (FE-SEM) and Fourier transform infrared spectroscopy (FTIR). Remarkably,  $\text{Fe}_2\text{O}_3$  has significant improvement on heat release rate (HRR), total heat release (THR), smoke factor (SF), and total smoke release (TSR) of the APP/WPC. SDT implied that  $\text{Fe}_2\text{O}_3$  played a positive role during burning and there is a synergistic effect of smoke suppressing for  $\text{Fe}_2\text{O}_3$  on APP/WPC. The LOI results showed that compared with samples without flame retardant, adding  $\text{Fe}_2\text{O}_3$  improved the LOI value of WPC. TG indicated that  $\text{Fe}_2\text{O}_3$  and APP played an effective role in the course of thermal degradation of WPC. And the SEM and FTIR showed that  $\text{Fe}_2\text{O}_3$  and APP played a role in ameliorating the residual carbon structure.

KEYWORDS: Smoke suppression, flame retardant, wood-polyurethane composites,  $\text{Fe}_2\text{O}_3$ , APP.

### INTRODUCTION

Wood flour or wood flakes dispersed in a polymer matrix forming wood plastic composites, which take an increasingly important role as building materials. And the application of WPC has largely increased because they are bio-composites and renewable materials (John and Thomas 2008). There are a large number of advantages in decking, railing, docks, landscaping timbers, and some automobile industries (Ashori 2013, Panthapulakkal and Sain 2006, Liu et al. 2009). However, due to the high heating value of polymer materials, particularly, smoke fog

and toxic gases instead of thermal damage more common cause death, WPC show a higher fire risk in comparison to wood (Stark et al. 2010, Kozłowski and Władyska-Przybylak 2008, Gann et al. 1994). In a number of cases, there are some difficulties in escaping from the fire and blocking fire crews trying to save trapped people due to smoke and toxic gases, which limited WPC into the building and furniture industry (Jiang et al. 2014, Cassuto and Tarnow 2003, Ye et al. 2014, Borysiak et al. 2006). So far, only a limited amount of statistics has been published on halogen-free flame retardancy and smoke suppression of wood-polyurethane composites (Stark et al. 2010). Improving fire retardant of WPC, particularly, smoke suppression is necessary.

Higher loading of ammonium polyphosphate (APP) is always proposed as efficiency of fire resistance, and APP has been well established for polyolefin polymers and WPC (Bourbigot et al. 2004, Garcia et al. 2009). Ammonium phosphate (APP) not only play part in the condensed phase but also could reduce the production of combustible fragment, meanwhile take effect in shaping a protective carbon layer for the phosphorus flame retardants (Montaudo et al. 1984). Particularly, taking into full account the impact on the environment, APP is the most frequently used flame retardant additive (Li and He 2004, Schartel et al. 2003). However, some papers have showed that the effect of adding APP as the flame retardant is better than other flame retardants, but the smoke and CO production is relatively higher than untreated samples (Seefeldt et al. 2012). Thus, it is the key to further explore high performance of flame retardants and smoke suppressants of WPC applications. Furthermore, the higher loading of APP led to higher cost and worse adhesion for the composites, especially, compared with the flame retardants containing bromine and metal hydroxides, APP additives have lower heat stability (Bourbigot et al. 2004, Montaudo et al. 1984, Shen et al. 2012). For all we know, no paper has been published about the synergistic smoke suppression and flame retardant effects between ferric oxide and ammonium polyphosphate on wood-polyurethane composites.

Iron compounds in the late years show much attention from the research teams because of its excellent flame retardancy and smoke suppression (Chen et al. 2014, Liu et al. 2015, Hassan 2004, Sharma 2003). And some scholars have studied the application of ferrocene in flame retardant and smoke suppressant on PVC composites (Carty et al. 1996). The experimental results showed that the ferrocene can catalyze into carbon and effectively reduce the activation energy of the system in the process of removing nitrogen. Other researchers also successfully compounded iron oxide, insoluble salts with polyphenylene oxide or zinc borate polystyrene from the flame retardant polyamide system. Research suggested that iron compounds increase the system LOI value. It not only enhanced the microstructure of the residual carbon layer after combustion, but also improved the heat stability of the system (Chen et al. 2015, Jiao et al. 2015, Weil et al. 2003).

In this work, ferric oxide ( $\text{Fe}_2\text{O}_3$ ) serve as synergistic flame retardant and smoke suppressant with APP for WPC. To explore whether  $\text{Fe}_2\text{O}_3$  could greatly improve the smoke suppression efficiency. And, the effect was investigated by CCT, SDT, LOI, and TGA, respectively. Furthermore, in order to further discuss the relationship between smoke suppression properties and the structure of carbon residue after cone calorimetric test, and to explore the mechanism of synergistic flame retardancy and smoke suppression characteristics by using photographs of carbon residue, FE-SEM and FTIR. The aim of this paper was to explore the effective method of flame retardant and smoke suppression for wood polyurethane materials.

As noted previously, some researchers have studied the flame retardant of  $\text{Fe}_2\text{O}_3$  and APP in polymers. Nevertheless, there is no literature which is obtainable to research the influence of synergistic flame retardancy and smoke suppression between  $\text{Fe}_2\text{O}_3$  and APP on wood-polyurethane composites. Therefore, this article was devoted to research the mechanism of synergistic flame retardant and smoke suppression  $\text{Fe}_2\text{O}_3$  and APP on wood-polyurethane composites.

## MATERIAL AND METHODS

### Materials

Poplar flour (PF) was purchased from a sawmill in Hebei province, China.

PF sieved by 40–60 mesh sieve and then dried at  $105 \pm 5^\circ\text{C}$  in the oven until constant weight. Polyurethane foam sealant (PUF), with the expansion ratio of 78 was used as the polymer matrix, which obtained from Shanghai Duanchuang Building Material Co., Ltd., China. The silane coupling agent (KH-550) was supplied by Jinan Xing Feilong Chemical Co.Ltd., China. The starch adhesive was obtained by Hangzhou Jia Lifeng Investment Co., Ltd., China. The ferric oxide ( $\text{Fe}_2\text{O}_3$ ) was analytical reagent AR and was purchased from Jinke Fine Chemical Research Institute (Tianjin, China). Ammonium polyphosphate (APP, phase II, the degree of polymerization >1000) was obtained from Shenzhen Jingcai Chemical Co. Ltd., China.

### Preparation of WPC

According to a certain weight percent (wt%) as shown in Tab. 1 of poplar flour (PF), starch adhesive, polyurethane foam sealant (PUF), silane coupling agent (KH-550), ferric oxide ( $\text{Fe}_2\text{O}_3$ ), ammonium polyphosphate (APP) stirring in the container by precision force electric mixer and the mixture was stirred to even color. Finally, samples were put into a model with different size, and then put them in the drying oven at  $600^\circ\text{C}$  for 60 min.

Tab. 1: Composition of investigated WPC materials.

Sample code	PF (wt%)	PUF (wt%)	KH-550 (wt%)	Amylan (wt%)	$\text{Fe}_2\text{O}_3$ (wt%)	APP (wt%)
WPC-0	40	60	3	4	0	0
WPC-1	32	48	3	4	0	20
WPC-2	32	48	3	4	1	19
WPC-3	32	48	3	4	2	18
WPC-4	32	48	3	4	3	17
WPC-5	32	48	3	4	20	0

### Measurements

#### *Cone calorimeter test (CCT)*

The combustion behavior of WPC was carried out with a cone calorimeter (Made in British, instrument model FTT 0006) in accordance with ISO 5660. Each specimen was  $100 \times 100 \times 9$  mm size. The test samples were wrapped in aluminum foil covering the sides and the bottom at a heat flux of  $50 \text{ kW}\cdot\text{m}^{-2}$  and three replicate specimens were tested for each group.

#### *Smoke density test (SDT)*

The smoke properties were gauged by a JCY-2 smoke density test machine (China) according to ASTM D2843. Each specimen with the dimension of  $25 \times 25 \times 6$  mm was placed on a stainless steel grid.

#### *Limiting oxygen index (LOI)*

The limiting oxygen index is measured by LFY-605 automatic oxygen index tester (Textile Science Research Institute of Shandong Province, China) according to ISO 4589. The size of the samples used for the test was  $100 \times 10 \times 4$  mm.

*Thermogravimetric analysis (TGA)*

TGA was conducted on a ZRY-1P thermal analyzer (Tian Mei, China). The nitrogen flow ratio of thermal analyzer was under  $50 \text{ mL}\cdot\text{min}^{-1}$  and the temperature increased from ambient temperature to  $750^\circ\text{C}$  at a heating rate of  $200^\circ\text{C}\cdot\text{min}^{-1}$ . Before the experiment, the samples were ground into powder and the weights of powder between 5mg to 8mg. Two replicates were tested for each sample.

*Field emission scanning electron microscope (FE-SEM)*

The surface micrographs of residues after cone calorimetry tests were examined using FE-SEM (Japan, instrument model JSM-7001F).

*Fourier transform infrared spectroscopy (FTIR)*

The residues for WPCs after cone calorimetry tests and potassium bromide (KBr) were grounded into powders by agate mortar, and each admixture extruded into a circular slice. The FTIR spectra were examined by a spectrum 100D of spectrometer (Perkin Elmer, British).

## RESULTS AND DISCUSSION

### Cone calorimeter test

*Heat release rate (HRR)*

Fig. 1 demonstrates the heat release rate (HRR) of cone calorimeter measures for WPC with the differentiation of APP and  $\text{Fe}_2\text{O}_3$  for comparison. Peak heat release rate (PHRR) is one of the most significant factors to access the fire security (Chen et al. 2015). During the progress of the CCT, the increase rapidly of the first PHRR for every specimen can be put down to combustion of WPC could release the volatiles. WPC-0 without any flame retardant additive is the highest PHRR. While for WPC-3, the PHRR of the maximum decrease from  $486.3 \text{ kW}\cdot\text{m}^{-2}$  to  $292.8 \text{ kW}\cdot\text{m}^{-2}$ , which is approximately 39.8% lower than that of WPC-0. For WPC-1, WPC-2, WPC-4, WPC-5, the PHRR decreased by 37.4%, 33.6%, 33.7%, and 2.3%, respectively. Thus it can be seen that the PHRR was improved much better because of adding  $\text{Fe}_2\text{O}_3$  and APP. It may obtain the conclusion that  $\text{Fe}_2\text{O}_3$  and APP work basically as a heat transfer protective screen from the heat producer to the composites, which prevent WPC further oxidation. In particular, when adding  $\text{Fe}_2\text{O}_3$  to the WPC/APP system, further lower the PHRR value. The outcomes indicated that  $\text{Fe}_2\text{O}_3$  has a great flame retardant synergism effect with APP for WPC, particularly, the most effective was appeared in WPC-3 with 2wt%  $\text{Fe}_2\text{O}_3$  and 18%APP.

The combustion performances of WPC with different ratio APP and  $\text{Fe}_2\text{O}_3$  were quite different. When comparing the efficiency of APP and  $\text{Fe}_2\text{O}_3$  between WPC-0, WPC-1 and WPC-5, it can be seen that APP took an important part in catalysis of forming carbon residue and was an effective fire retardant. When  $\text{Fe}_2\text{O}_3$  and APP added into WPC, the HRR of WPC decline rapidly after the first PHRR and a slow peak was observed at 110-250 s, which should be connected with an increasing barrier due to residue formation. Furthermore, the value of heat release rate decreasing can be interpreted as endothermic decomposition of APP and  $\text{Fe}_2\text{O}_3$  under thermal behavior, which in turn advanced the energy run away from the system. This would be propitious to form protective char layers of WPC with APP and  $\text{Fe}_2\text{O}_3$ . This might be attributable to  $\text{Fe}_2\text{O}_3$  can help char residue in the compact, expansion degree and mass during the cone calorimetry (Babrauskas and Peacock 1992, Wang et al. 2008, Qian et al. 2013).

Two peaks of WPC-0 can be thought of as a characteristic feature as wood plastic composites by identifying the HRR curve. The first PHRR is a material property. WPC additionally effected a peak at the end, which is caused by barrier formation due to the production of char. The heat release rate curves inclined to a relatively stable state, and samples formed efficient protective carbon layer after the first peak (Fig. 1). The second peak form because of the gradual degradation of the protective carbon layer as the char surface burning out of the whole sample, and then the formation of a new protective char in virtue of the flame retardant (Schartel and Hull 2007).

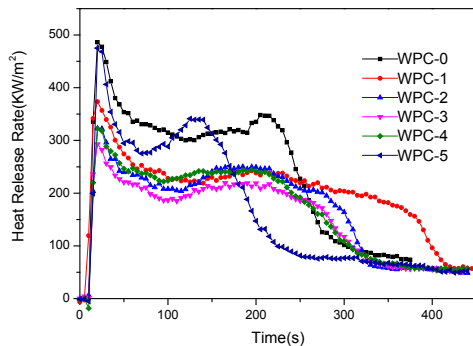


Fig. 1: Heat release rates of WPC at a flux of  $50 \text{ kW}\cdot\text{m}^{-2}$ .

#### Total heat release (THR)

The result of time-total heat release curves is shown in Fig. 2, and adding two kinds of fire retardants into WPC with a lower THR compared with the composites with only one fire retardant. WPC containing APP and  $\text{Fe}_2\text{O}_3$  have caused the best improvement of the total heat release about 20%. Beyond that, the THR value of WPC decline further after adding  $\text{Fe}_2\text{O}_3$ , which is a cause of in tumescent and pyknotic carbon residue on the ignition burning surface of the specimen limiting flame propagation. WPC-2, WPC-3 and WPC-4 with different proportions of APP and  $\text{Fe}_2\text{O}_3$  show similar changes in the THR. The total heat release value of WPC-0 is  $92.6 \text{ MJ}\cdot\text{m}^{-2}$  at 375s while WPC-1 is reduced to  $84.5 \text{ MJ}\cdot\text{m}^{-2}$ , which reduced by 8.7%. The THR value of WPC-5 is higher than that of WPC-1 between 40 and 260 s, which suggests that  $\text{Fe}_2\text{O}_3$  helps to improve the pyrolysis process of WPC. WPC-1 formed a compact carbon residue shell with higher expansion during the pyrogenation process, leading lower THR compared to WPC-5. When the burning time after 400s, the THR value of WPC-5 is lower than WPC-1. The reason is that the pyknotic carbon layer of WPC-1 was destroyed during the period of combustion.

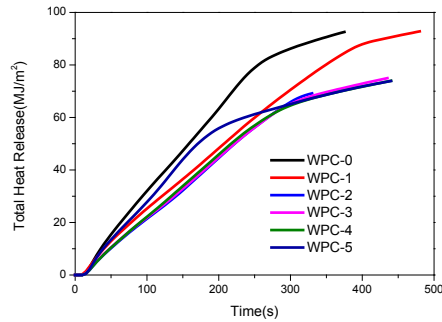


Fig. 2: Total heat releases of WPC composites at a flux of  $50 \text{ kWm}^{-2}$ .

### Mass loss

The mass loss-time curves of WPC with different fire retardants are exhibited in Fig. 3. The mass loss action may have relations with the heat release and smoke production. It can be seen that the mass of WPC-0 without the addition of any fire retardant is the lowest, just 21.86 % remained at 370 s. However, there is about 37.68% char residue of WPC-1 at the end of the test, which is lower than the residue of 41.8% from the WPC-5. This can be illustrated that APP can produce ammonia, and created an expansive carbon layer on the surface of WPC as a physical protective screen to block heat and quality transfer. At the same time, the residual carbon layer would keep oxygen from entering the bottom of the material and might produce a lower volatility. When  $\text{Fe}_2\text{O}_3$  is added to APP/WPC, the mass is higher than WPC-1. This result was expected, because  $\text{Fe}_2\text{O}_3$  can emerge  $\text{Fe}^{+}$ . Due to the presence of polyvalent iron, which can alter the structure of carbon residue in the cone calorimetry. Moreover, APP reacts with  $\text{Fe}^{+}$  as bridges, which would raise weight and steadiness of APP (Zhang et al. 2009).

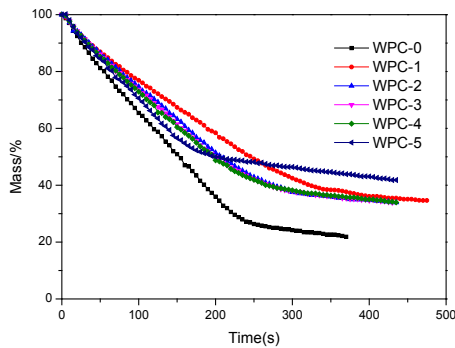


Fig. 3: Mass loss curves of WPC composites at a flux of  $50 \text{ kWm}^{-2}$ .

### Total smoke release (TSR)

Production and emission of smoke and toxic gases is one of the most important parameters representing the fire risk concerned composites (Nikolaeva and Kärki 2016). Fig. 4 presents the TSR curves of WPC in the cone calorimetry experiments. WPC-0 and WPC-1 with higher TSR values are  $3736.4 \text{ m}^2\cdot\text{m}^{-2}$  and  $2467.6 \text{ m}^2\cdot\text{m}^{-2}$  at the end, respectively than other composites. Actually, the WPC was catalyzed by APP broken down in to the polyphosphoric acid to produce

more smoke factors, which is a cause that makes WPC-1 the value of TSR curves higher. But the lowest TSR value is WPC-5 ( $1820.9 \text{ m}^2\cdot\text{m}^{-2}$ ), which reduced by 51.3% in comparison with WPC-0. That proves that  $\text{Fe}_2\text{O}_3$  contributes to forming the dense residual carbon layer and keep sinflammable gases and smoke particulates from dispersing into the environment (Carty et al.2001, Carty and White 2002). It can conclude that  $\text{Fe}_2\text{O}_3$  acts as very important roles in reducing TSR values. Compared to WPC-1, the value of TSR further decreased while adding  $\text{Fe}_2\text{O}_3$  into APP/WPC. And it is likely to be due to the protection of char layer, the TSR values of WPC-2, WPC-3 and WPC-4 is fallen by 35.6%, 34.8%, 38.2%, separately. It is concluded that  $\text{Fe}_2\text{O}_3$  as a synergistic smoke suppressant with obvious effect on ammonium polyphosphate-wood polyurethane composites. As can be seen from the Fig. 4, by adding  $\text{Fe}_2\text{O}_3$  into APP/WPC generate a more compacted carbon layer which can availably reduce the production of smoke particulates which can make the value of TSR lower.

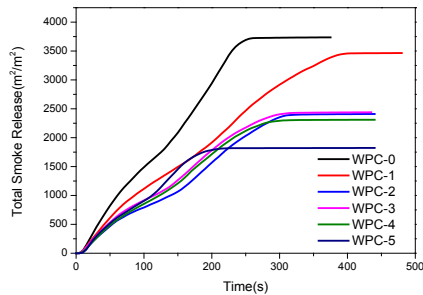


Fig. 4: Total smoke release of WPC at a flux of  $50 \text{ kW}\cdot\text{m}^{-2}$ .

### Smoke factor (SF)

Fig. 5 shows the SF curves for all samples, which is the product of PHRR and TSR (Ricciardi et al. 2012). SF is used to evaluate the release smoke rate is as a more accurate measure (Chen et al. 2015). It can be seen that the SF value of WPC-1 containing only APP is decreased to  $608.7 \text{ MW}\cdot\text{m}^{-2}$  (reduce by 45.9%) while WPC-0 is  $1126.0 \text{ MW}\cdot\text{m}^{-2}$ . It is crystal clear that the addition of flame retardant significantly reduces the SF values of WPC. Furthermore, the samples containing both APP and  $\text{Fe}_2\text{O}_3$  show further decrease in SF values compared with WPC-1 with only APP. The SF value of WPC-2, WPC-3 and WPC-4 is  $445.2 \text{ MW}\cdot\text{m}^{-2}$ ,  $414.0 \text{ MW}\cdot\text{m}^{-2}$  and  $440.0 \text{ MW}\cdot\text{m}^{-2}$ , respectively, which is approximate and WPC-3 is better than WPC-2 and WPC-4. As with the above results, the presence of  $\text{Fe}_2\text{O}_3$  further decreases the smoke generation.

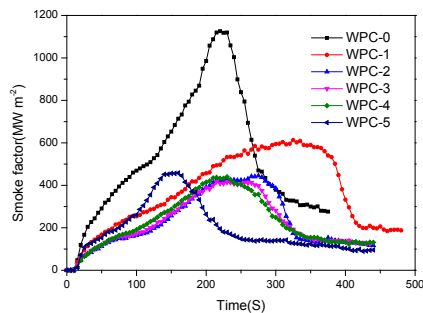


Fig. 5: Smoke factors of WPC at a flux of  $50 \text{ kW}\cdot\text{m}^{-2}$ .

### Photographs of carbon residue

The pictures of char residues after the WPC burned in cone calorimetry experiments at Fig. 6. Compact carbon layer could prevent transferring heat from flame zone to flame basement and defend the substrate materials from further burning or pyrogeneration of WPC. As displayed in Fig. 6, it is obviously that WPC-0 became the lightest and loosest char residue, especially, WPC-0 complete combustion. The photograph of WPC-0 is in accordance with the highest HRR and largest mass loss. The appearance of the residual carbon was closely connect with the burning properties of WPC. Compared with WPC-1, WPC-2, WPC-3 and WPC-4, WPC-0 and WPC-5 did not form hard residual carbons and completely burned to form ash. Besides, when  $\text{Fe}_2\text{O}_3$  and APP were added into wood plastic materials, the carbon layers became coherent and compact after cone.

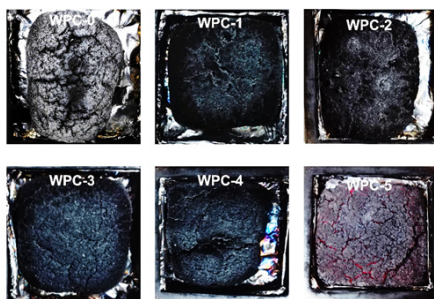


Fig. 6. Photographs of char residues of WPC after CCT.

### Smoke density test (SDT)

The smoke density test can reveal details about the smoke production. Fig. 7 shows the smoke density curves of flame retardant wood-plastic composites in the smoke density test. The curve of WPC-5 shows the similar trend as that of WPC-0 with untreated composite, whereas the smoke of WPC-5 is much less than that of untreated. Compared to WPC-5, the smoke density reduces from 33.8 to 12.5% at the end of the experiments, which is about 63.0% lower than that of WPC-0. In the case of WPC-0, we can conclude that the release of smoke rapidly increases in the first 15 s and gets the highest smoke density (54.7%) and decreases gradually after 15s. The smoke density mainly increases, and it attains the maximum value (65.1%) at 144 s in the smoke density test. This implies that the smoke density of only incorporating  $\text{Fe}_2\text{O}_3$  is obviously less than that of untreated. Here, the addition of  $\text{Fe}_2\text{O}_3$  in wood-plastic composites reduce the smoke production of wood plastic composites and takes a passive effect on the process of the formation of smoke factors.

WPC with only APP, the smoke density of the samples increased rapidly. It is concluded that WPC-1 with only APP produced much smoke at the first 150 s. However, after that the smoke density of WPC-1 rapidly reduces. This can be interpreted that APP can generate smoke precursors and form residual carbon shell by decomposing at low temperature. The smoke precursors resulted in highest smoke density at the first 150s. On the other hand, the smoke density in WPC-1 is higher than others, which may be due to APP as flame retardant inhibit combustion producing much smoke. Likewise, the smoke density curves of smoke density test WPC-1, WPC-2, WPC-3 and WPC-4 show the similar trend, and the smoke density values are depressed with the increase the addition of  $\text{Fe}_2\text{O}_3$ . And WPC-4 shows the lowest smoke density value demonstrating that  $\text{Fe}_2\text{O}_3$  combined with APP could significantly decrease the smoke production to a great extent. It is concluded that  $\text{Fe}_2\text{O}_3$  have smoke suppression performance for



APP/wood polyurethane composites. Therefore it can be obtained that the proper proportion of  $\text{Fe}_2\text{O}_3$  is favorable for improving the structure of the residual carbon in the smoke density test.

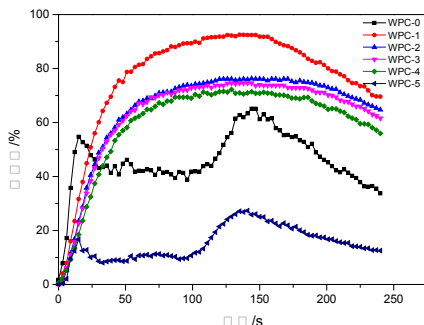


Fig. 7: smoke density curves of wood-plastic composites.

### Limiting oxygen index (LOI)

The limiting oxygen index test is used to check the minimum oxygen concentration required for burning. As can be seen from Fig. 8, in contrast to WPC-0 the limiting oxygen index value of WPC-1 is available promoted.

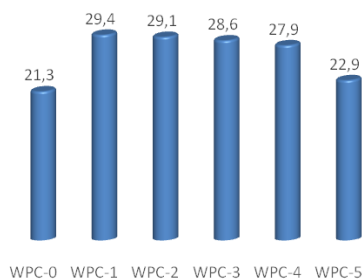


Fig. 8: Limiting oxygen index for WPC.

The LOI value of the WPC-0 is only 21.3, but the LOI value of WPC-1 with 20.0 wt% APP is as high as 29.4. This illustrates the flame retardant effect of APP is fairly satisfactory. Compared with WPC-1, the LOI of WPC/APP/ $\text{Fe}_2\text{O}_3$  composites decrease slightly. The lower LOI value might have been due to pyrophosphate compounds is produced by the reaction between  $\text{Fe}_2\text{O}_3$  and polyphosphoric acid which the decomposition of APP. The LOI value of WPC-5 with 20.0wt%  $\text{Fe}_2\text{O}_3$  is 22.9, which is still higher than that of WPC-0 and lower than WPC-1. The above phenomena imply that  $\text{Fe}_2\text{O}_3$  can improve the flame retardant effect on WPC, but may be due to that ferrous powder particles aggregated severely, suggesting poor dispersibility. When the  $\text{Fe}_2\text{O}_3$  content is raised,  $\text{Fe}_2\text{O}_3$  could alter residual carbon expansion degree and density.  $\text{Fe}_2\text{O}_3$  resulted in released more flammable gas. Thus, the addition of  $\text{Fe}_2\text{O}_3$  led to a slightly lower the LOI value of APP/WPC. So, the LOI values of WPC-2, WPC-3 and WPC-4 are lower than that of WPC-1. It is concluded that APP and  $\text{Fe}_2\text{O}_3$  still achieve a good flame retardancy on ameliorating LOI value of WPC. The results of the limiting oxygen index test also proved the flame resistance properties of APP and  $\text{Fe}_2\text{O}_3$  on WPC.

### Thermogravimetric analysis (TG)

The thermal stability of the flame-retardant WPC is an essential parameter for the working and application of materials. Fig. 9 is the TG and its DTG curves of wood-polyurethane composites filled with different ratio of  $\text{Fe}_2\text{O}_3$  and APP exposed on nitrogen atmosphere. Tab. 2 sums up analysis from the thermogravimetric tests containing the initial temperature of pyrolytic degradation ( $T_{\text{initial}}$ ), the peak temperature of heat degradation ( $T_{\text{peak}}$ ), and the remaining residual carbon at 750°C.

Tab. 2: TG results of WPCs based on different ratio of  $\text{Fe}_2\text{O}_3$  and APP.

Sample code	$T_{\text{initial}}$ (°C)	$T_{\text{peak}}$ (°C)	Residues (wt%)
WPC-0	256.3	294.1	32.3
WPC-1	251.1	301.1	55.0
WPC-2	260.8	303.4	60.7
WPC-3	268.6	303.6	65.0
WPC-4	261.6	298.8	60.6
WPC-5	260.8	267.3	67.4

When the temperature is below 250°C, weight loss decrease among all the samples (Fig. 9). This is a result of the loss of moisture. The TG of WPC-0 initial decomposition temperature at 256.3°C and the maximum weight loss temperature is 294.1°C (Tab. 2). The beginning decompose temperature of WPC-1 containing APP is 251.1°C, which is lower than WPC-0. This could be explained by the low decomposition temperature of APP, which promotes WPC thermal degradation at a lower temperature. Adding APP into WPC can keep materials from further thermal degradation. In the case of the samples from WPC-2 to WPC-5, the degradation temperature in the composites containing the  $\text{Fe}_2\text{O}_3$  are 260.8, 268.6, 261.6, and 260.8°C, respectively. Compared with WPC-1, another important feature observed was the higher initial degradation temperature of the samples containing  $\text{Fe}_2\text{O}_3$  in the composites. This indicates that the thermal stability of the WPC improved after using ferric oxide.

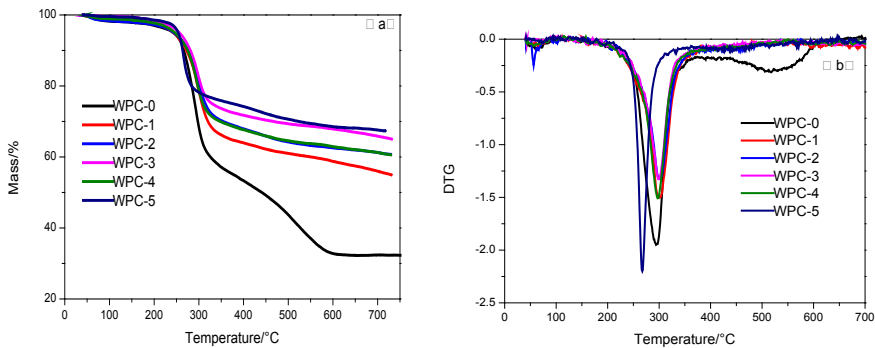


Fig. 9: TG and DTG curves of WPC.

DTG curves showed that in the main pyrolysis stage, the DTG peak temperature of WPC filled with APP and ferric oxide forming a slightly higher temperature compared WPC-0, all of these proved that APP and  $\text{Fe}_2\text{O}_3$  can restrain the pyrolysis of WPC. This shows that WPC with APP and  $\text{Fe}_2\text{O}_3$  has the function of catalytic charring. In addition, the TG of WPC-1

left about 55.0 wt%, which is higher than that of WPC-0 (32.3 wt%). Moreover,  $\text{Fe}_2\text{O}_3$  further increases the weight of APP/WPC at high temperature, which is the same reason as mentioned former part of this article. The residues of WPC-2, WPC-3 and WPC-4 are about 60.7, 65.0 and 60.6 wt% at the end, respectively. The presence of  $\text{Fe}_2\text{O}_3$  could enhance the heat endurance of WPC and promote the formation of carbon layer, which is more stability than WPC-1. The presence of  $\text{Fe}^{n+}$  does lead to some radical trapping, which can also enhance thermal stability (Kong et al. 2005). This means  $\text{Fe}_2\text{O}_3$  contributes to effective flame retardancy and form more stable carbon layers during combustion processes. WPC-3 has the biggest improvement of thermal stability. This might be attributed to the presence of a synergistic effect of APP and  $\text{Fe}_2\text{O}_3$  which hampered the decomposition of volatile products.

### Field emission scanning electron microscope (FE-SEM)

Fig. 10 is the SEM of char residues of all samples after CCT. The residual carbon surface of WPC-0 was broken and discontinuous, which is due to lots of smoke destroyed carbon layer rupture.

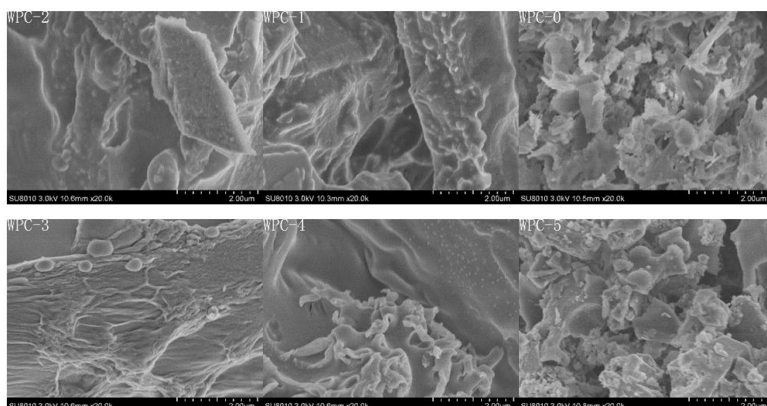


Fig. 10: SEM of char residue of WPC after CCT.

And WPC-5 has loose char residues, but WPC-5 showed better smoke suppression which due to  $\text{Fe}_2\text{O}_3$  can lead to the formation of highly reactive free radical reactions in the gas phase, and then free radicals can oxidize the smoke particles to CO, the reaction formula is  $\text{C}(s) + \text{OH}\cdot \rightarrow \text{CO} + \text{H}$ . Char surface structure of WPC-1 with only adding APP improved, but the carbon layer presents an irregular appearance and some fault cracking phenomenon, this is because the APP has good flame retardant effect to form a carbon layer, but the smoke suppression effect is relatively poor, this result is consistent with the front. Carbon residue of samples with adding APP and  $\text{Fe}_2\text{O}_3$  showed a dense carbon layer, which APP and  $\text{Fe}_2\text{O}_3$  can inhibit combustible gas and smoke release, isolate oxygen and improve flame retardancy and smoke suppression of WPC. Particularly, WPC-3 has the densest carbon layer surface in all specimens, which is also consistent with lowest HRR, which shows that the addition of  $\text{Fe}_2\text{O}_3$  contributes to the formation of cross-linked char structure and inhibits heat transfer and gas generation.

### Chemical compositions of char residues

Fig. 11 shows spectra of the combusted residues of WPC after cone calorimeter test. A broad and strong absorption peak near  $3400\text{ cm}^{-1}$  was attributed to the -OH stretching vibration that

was formed in all the combusted residues, this showed that may produce inorganic compounds containing hydroxyl by combustion.

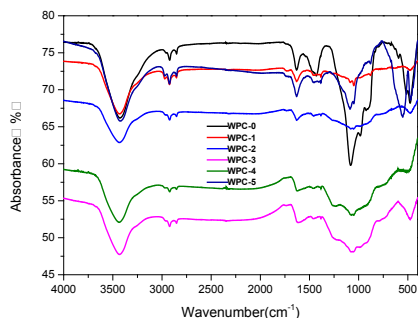


Fig. 11: FTIR spectra of char residues after CCT.

The appearances of peaks between 2800 and 3100  $\text{cm}^{-1}$  of all samples, probably due to the presence of carbon bonds, indicating that there were still some organic matter after combustion. The characteristic peak at 1630  $\text{cm}^{-1}$ , probably because of potassium bromide containing water. Particularly, only WPC-0 after combustion with a pronounced peak at 1429  $\text{cm}^{-1}$ , which may be due to  $\text{CH}_2$  shear vibration (cellulose) or  $\text{CH}_2$  flexural vibration (lignin) (Cheng et al. 2016), indicating that the combustion of WPC-0 is complete. 1050  $\text{cm}^{-1}$  belongs to the C-O stretching vibration which has generated aliphatic alcohols in the heat treatment process. The absorption peak of the samples with two kinds of flame retardant is not obvious at 1050  $\text{cm}^{-1}$  because the ions can catalytic oxidation the product without fully burning, and made the removal reaction of hydroxyl group and methyl group, and polycyclic aromatic hydrocarbons go deeper. This fully demonstrates that  $\text{Fe}_2\text{O}_3$  and APP are effective synergistic flame retardants for polyurethane-wood composites.

## CONCLUSIONS

This paper studied the synergistic flame resistance and smoke suppression properties of APP and  $\text{Fe}_2\text{O}_3$  on WPC by methods of CCT, SDT, LOI, TG, SEM and FTIR. The following conclusions are drawn below such research. The proportion of APP and  $\text{Fe}_2\text{O}_3$  shows an effectually better synergistic effect of flame retardancy and smoke suppression on WPC by the data of HRR, LOI, TG and photographs of carbon residue.  $\text{Fe}_2\text{O}_3$  can not only improve the structure of residual carbon layers which restrict the smoke production but also has excellent effects on smoke suppression properties for APP/WPC.

## ACKNOWLEDGEMENTS

This work was financially supported by The Fundamental Research Funds for the Central Universities (NO. 2016ZCQ01) and the National Natural Science Foundation of China (Project 51779005/E090301).

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