A NOVEL FIRE RETARDANT AFFECTS FIRE PERFORMANCE AND MECHANICAL PROPERTIES OF WOOD FLOUR-HIGH DENSITY POLYETHYLENE COMPOSITES

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Wood flour-high density polyethylene (HDPE) composites were prepared to investigate the effects of ammonium polyphosphate based fire retardant content (2, 4, 6, 8, and 10-wt%), on the flammability, mechanical, and morphological properties of the wood flour-HDPE composites in this study. Cone calorimetry analysis showed that the addition of fire retardant could decrease the heat release rate (HRR) and total smoke release of wood flour-HDPE composites, while it had no obviously effects on effective heat of combustion. Most of the decrease of the HRR occurred with the concentration of the fire retardant up to 4-wt%. With addition of fire retardant, the composites showed a decrease in tensile elongation at break and impact strength, and had no obvious effect on tensile and flexural strength. The scanning electron microscopy observation on the fracture surface of the composites indicated that fire retardant had a uniform dispersion in the wood flour-HDPE composites. However, interfacial bonding would be suggested to improve in wood flour-HDPE composites with ammonium polyphosphate based fire retardant.

Keywords: Fibers; Wood-plastic composites; Mechanical properties; Ammonium polyphosphate (APP)-based flame retardant

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INTRODUCTION

In recent years, polymer composites reinforced with natural fiber, such as wood, corn stalk, flax, hemp wheat straw, newspaper fiber, sunflower stalk, and bagasse fiber, have become popular due to their renewability, recyclability, and biodegradability (Oksman and Clemons 1998; Pan et al. 2008; Ashori and Nourbakhsh 2009; Ashori 2010). The utilization of natural fibers as an alternative to synthetic fiber for polymer composites can reduce the consumption of synthetic fiber and thus help protect forests and the environment. These value-added products have a unique combination of excellent durability, superior dimensional stability, high rigidity, and relatively low density (Bledzki and Faruk 2003; Hristov et al. 2004; Zhang et al. 2006). Due to their superior properties, these products are now widely used as interior automotive panels, garbage pails, crates, lawn, garden equipment, and especially in decking.

The addition of natural fibers to a polymer matrix can change the mechanical properties of polymer composites. Besides the main properties for structure materials, mechanical properties and the material costs, for many applications, flammability is one of the important parameters that often limit the application of composites to building industry and vehicles (Yap et al. 1991; Zhang and Horrocks 2003; Borysiak et al. 2006; Chang et al. 2007; Kozłowski et al. 2008). In order to improve fire behavior of natural fiber reinforced polymer composites, fire retardant agents, such as halogen, nitrogen, and phosphorus, have been introduced to the natural fiber and polymer system (Lu et al. 2004; Estevao et al. 2004; Simkovic et al. 2005).

The most commonly used is ammonium polyphosphate (APP) in natural fiber reinforced polymer composites. APP is a compound of the phosphorous-nitrogen synergism, which is known to intumesce. In a heated environment, APP will foam, creating a barrier that blocks heat and oxygen from the flammable surface, improving charring. APP also lowers smoke production, inhibits smoldering, and helps resist flame migration (Stark et al. 2010). Li and He (2004) established that APP was an effective flame retardant for linear low-density polyethylene (PE)-wood fiber composites and that it had an influence on impact strength of composites. García et al. (2009) presented fire retardancy of the PE-wood fiber composites affected with APP, and found that the addition of APP could lead to auto-extinguishing material. Schartel et al. (2003) explored the effects of the external heat flux on flammability of polypropylene-flax fiber composites with APP and expandable graphite. With increasing external heat flux from 30 to 70 kW/m^2, the heat release rates increased, while the burning time and time to ignition decreased. Gao et al. (2010) gave a more comprehensive insight into the mechanism of the PE-wood fiber film composites affected by the insoluble APP, and they concluded that the addition of insoluble APP increased surface activity of wood fibers and interface compatibility between wood fiber and PE under hot processes.

Studies evaluating APP for polymer composites reinforced with natural fiber have shown that flammability can be improved. However, it is important to give a comprehensive insight on the relationships between dispersion of fire retardant, flammability, and mechanical properties of the polymer composites. The objective of this study was to evaluate the dispersion of fire retardant, flammability, and mechanical properties of natural fiber reinforced polymer composites affected by the addition of APP-based fire retardant by scanning electron microscopy, cone calorimeter, and mechanical testing.

EXPERIMENTAL

Materials

The high density polyethylene (HDPE) used in this work was a homopolymer pellet, grade 5000S, $\rho = 0.95$ g/cm^3, melt flow index (MFI) 0.8 to 1.2 g/10 min (190°C/2.16 kg), kindly supplied by Sinopec Yangzi Petrochemical Company Ltd. Poplar wood flours for this study were kindly supplied from a plywood pilot and prepared with the screen system equipped with 60 and 80 mesh screens. 1-wt% talcum powder was used for lubricant. Fire retardant was supplied from Henan Forestever Wood Tech Co. Ltd (China). The commercial product was a mixture of APP and different synergistic materials. The phosphorus content was about 24-wt%, the nitrogen content was 21-wt%, and the molybdenum was 9-wt%, respectively (according to EN13501-1:2002). The decomposition temperature of this fire retardant was 250-260°C. The HDPE, wood flour, fire retardant, and lubricant were dried at 105°C to constant weight before processing. Compositions of wood flour-HDPE composites are summarized in Table 1 according to a previous article (Pan et al. 2009). Wood flour-HDPE composites with fire retardant were incorporated 70-wt% HDPE and 30-wt% wood flour. The weight ratio of fire retardant and lubricant was based on the whole weight of wood flour-HDPE composites.

Table 1. Composition of Wood Flour-HDPE Composition (%-by Weight)

Sample code	Conditions	HDPE	Wood flour	Fire retardant	Lubricant
1	P100	100	0	0	0
2	P100F6	100	0	6	1
3	P70W30	70	30	0	0
4	P70W30F2	70	30	2	1
5	P70W30F4	70	30	4	1
6	P70W30F6	70	30	6	1
7	P70W30F8	70	30	8	1
8	P70W30F10	70	30	10	1

Note: P=HDPE, W=Wood flour, and F=Fire retardant.

Processing of wood flour-HDPE composites

The HDPE, wood flour, fire retardant, and talcum powder were preblended in a mixer and then extruded using a two screw extruder with a length-to-diameter ratio *L/D* of 36. The barrel temperatures were 140°C (zone I, feeding), 130°C (Zone II, melting), 125°C (Zone III, pumping), and 161°C at die, respectively, and the screw speed was 55 rpm. The extrudate was granulated using a chipper setting at the die. Afterwards, the granules were molded into mechanical test specimens by an injection molder, Chen de plastics machinery, at a molding temperature of 140°C. For cone calorimeter test, the granules were compression-molded at 150°C for 4 min.

Flammability Testing

The flammability of the samples was evaluated with a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. An external heat flux of 50 kW/m^2 was applied. The specimen size for cone calorimeter test was 100 mm × 100 mm × 2.3 mm. All of the samples were measured in the horizontal position and the edge frame was used for all tests.

Mechanical Testing

Tensile properties of wood flour-HDPE composites were evaluated with a SANS CMT 6104 tester. The tensile properties were determined in accordance with the National Standards of the People's Republic of China GB/T 1040-1992 procedure at a crosshead rate of 2 mm/min. Six specimens were tested in each run.

Flexural tests of 80 × 10 × 4 mm test pieces were also performed with a SANS CMT 6104 tester. The flexural properties were determined according to the National Standards of the People's Republic of China GB/T 9341-2000 in the three point bending mode at a cross head speed of 2 mm/min with a span of 67.4 mm. Six specimens were tested in each run.

The unnotched Charpy impact tests of 80 × 10 × 4 mm test pieces were performed with a SANS ZBC 1251-1 tester. The impact properties were determined according to the National Standards of the People's Republic of China GB/T 16420-1996. Six specimens were tested in each run. All the tests were performed at 25 ± 2°C.

Scanning Electron Microscopy (SEM)

To better understand the diffusion of fire retardant in wood flour-HDPE composites, the fracture surfaces of the impact-tested samples were observed using a QUANTA 200 SEM (FEI Company) at an accelerating voltage of 20 kV. The surfaces were coated with gold before examination.

RESULTS AND DISCUSSION

Flammability Analysis

The flammability characteristics of wood flour-HDPE composites were analyzed by cone calorimeter, and the results of heat release rate (HRR), effective heat of combustion (EHC), total heat release (THR), mass loss rate (MLR), specific extinction area (SEA), yield CO (Y_{CO}), yield CO_2 (Y_{CO2}), time to ignition (TTI), and total smoke release (TSR) from cone calorimeter are summarized in Table 2.

Table 2 Summary of Cone Calorimetry Analysis of Wood Flour-HDPE Composites

Conditions	HRR*^{1} kW/m^2	EHC^2 MJ/kg	THR^3 MJ/m^2	TTI^4 s	MLR^5 g/s	SEA^6 m^2/kg	Y_{CO}^{7}×100 (kg/kg)	Y_{CO2}^{8}×100 (kg/kg)	TSR^9 m^2/m^2
P100	172.12	19.43	32.71	43	0.08	161.74	1.86	162.8	276.44
P100F6	132.07	31.56	52.83	15	0.04	211.69	3.69	280.2	354.33
P70W30	194.20	28.20	70.89	28	0.06	178.50	3.72	230.2	452.02
P70W30F2	167.48	27.26	70.35	23	0.05	274.57	3.51	229.6	720.24
P70W30F4	123.28	27.53	45.61	25	0.04	212.96	4.71	251.9	352.90
P70W30F6	155.03	27.86	52.81	27	0.05	195.16	3.81	238.0	379.49
P70W30F8	148.13	27.69	61.48	25	0.05	147.98	3.88	237.8	363.21
P70W30F10	222.57	21.65	62.34	19	0.09	113.28	2.03	166.7	343.85

*^{1} HRR-heat release rate, ^{2} EHC-effective heat of combustion, ^{3} THR-total heat release, ^{4} TTI-time to ignition, ^{5} MLR-mass loss rate, ^{6} SEA-specific extinction area, ^{7} Y_{CO}-yield CO, ^{8} Y_{CO2}-yield CO_2, and ^{9} TSR- total smoke release

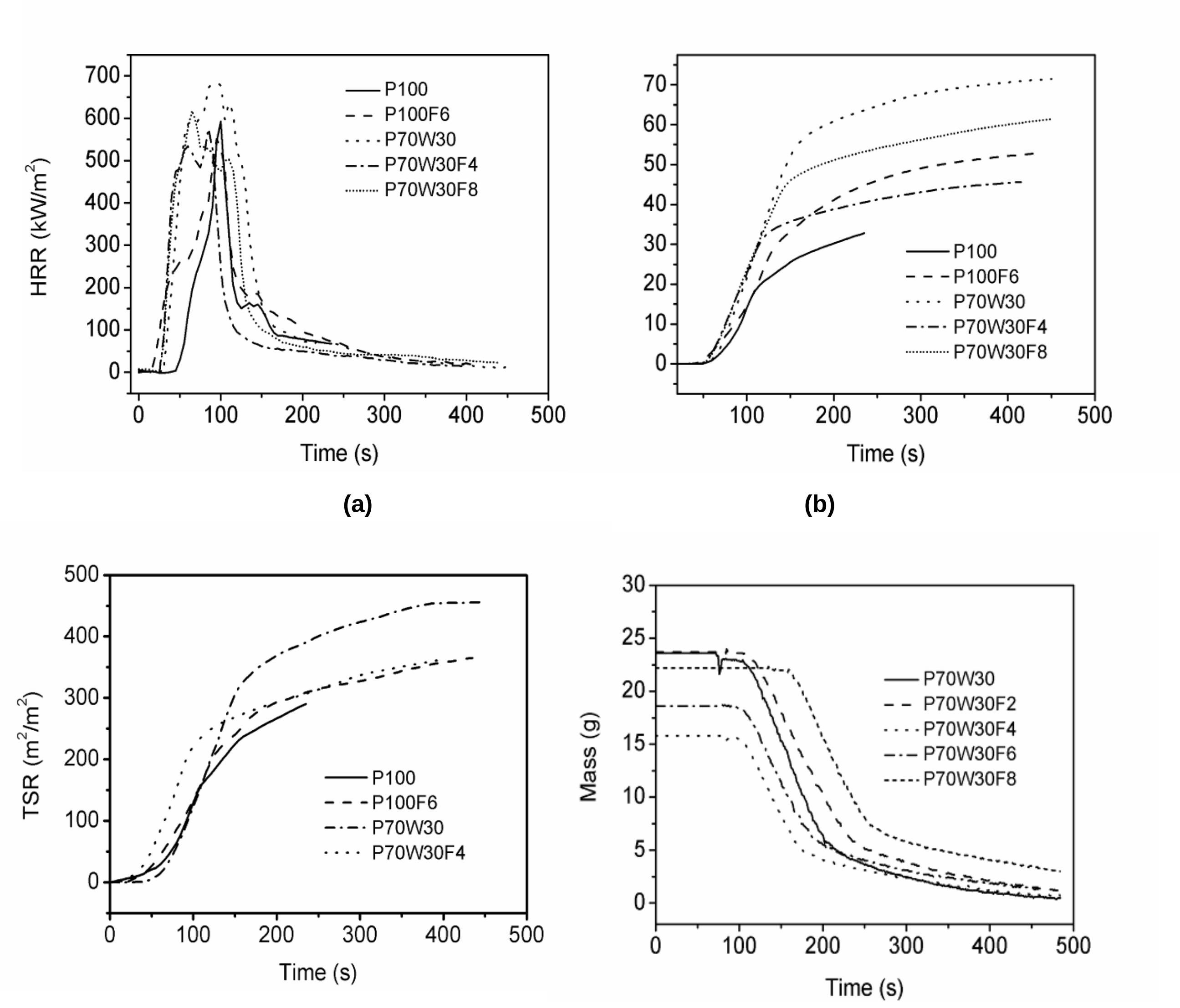
Generally, neat HDPE started dripping when the flame was in contact with the material, and the integrity of the material was completely lost immediately. The addition of wood flour could improve this behavior, and the composite maintained its integrity during the whole experiment. Furthermore, the wood flour reduced the mass loss rate (MLR) of the polymer by 25%, as shown in Table 2. This was probably due to the lignocellulosic structure of the wood flour (Schartel et al. 2003). Introducing wood flour to the polymer resulted in an increase in the heat release rate (HRR) by 12.8%, effective heat of combustion (EHC) by 45.1%, and total heat release (THR) by 116.37%, respectively. Specific extinction area (SEA) was slightly increased, and CO and CO_2 yield dramatically increased. Schartel et al. (2003) reported that the evolution of CO and smoke are the important hazard to life during a fire. It is well known that wood is a flammable material, and consequently its presence increases the fire risks of the wood flour-HDPE composites.

Figure 1(a, b) shows the flammability of neat HDPE and composites affected by fire retardant content. With increasing fire retardant content up to 8-wt%, the HRR of wood flour-HDPE composites decreased to 148.13 kW/m^2, which was approximately 23.7% lower than that of the composite material without fire retardant. This could be attributing the fact that the main component of fire retardant prevented oxygen to set fire by releasing phosphoric acid, which esterifies with hydrogen groups and acted as heat sinks by forming a protective layer as a coating. The results also showed that wood flour-HDPE composites with 4-wt% fire retardant decreased HRR by 36.5% and THR by 35.7%, respectively, mainly due to better diffusion of fire retardant on wood flour-HDPE composites. Furthermore, with increasing fire retardant from 0 to 8-wt%, the overall HRR decreased significantly, while EHC exhibited no obvious affect by the addition of fire retardant. It is reported that phosphorous compounds redirect decomposition reactions in favor of reactions yielding carbon over carbon monoxide or carbon dioxide. It is formation of a protective surface layer of char that inhibits access to oxygen (Stark et al. 2010). This result indicated that APP based fire retardant acted as a condensed phase fire retardant in wood flour-HDPE composites.

The release of incomplete combustion products, such as smoke and CO, was also detected and evaluated. On the one hand, they could provide a ranking in terms of fire hazards; on the other hand, they might support the analysis of fire retardancy mechanisms (Braun et al. 2007). Figure 1c shows the total smoke release (TSR) of wood flour-HDPE composites affected by fire retardant. It shows that the addition of fire retardant to HDPE composites reduced the total smoke emission. However, the addition of fire retardant had no obviously effect on CO and CO_2 production rate of the wood flour-HDPE composite. During the pyrolysis and combustion of composites, fire retardant could absorb a lot of heat in thermal decomposition, and then reduce the temperature of the composites. Consequently, fire retardant played an important role on smoke suppression of polymer composites.

Figure 1d shows the mass loss of wood flour-HDPE composites. It can be seen that the addition of fire retardant to wood flour-HDPE composites decreased the mass loss of system. The smallest mass loss was observed on wood flour-HDPE composites with 4-wt% fire retardant. Indeed, since PE was combusted with no significant residues, the wood flour was the origin of the residue.

Ignition is one of key features in respect to fire hazards. In Table 2, it can be seen that the incorporation of fire retardant to the neat HDPE can significantly reduce the time to ignition from 43 s to 15 s, and the addition fire retardant could slightly decrease the time to ignition of wood flour-HDPE composites. This was consistent with a previous study reported by Zhao et al (2009). This phenomenon could be explained by the relatively low thermal stability of fire retardant compared with that of HDPE.



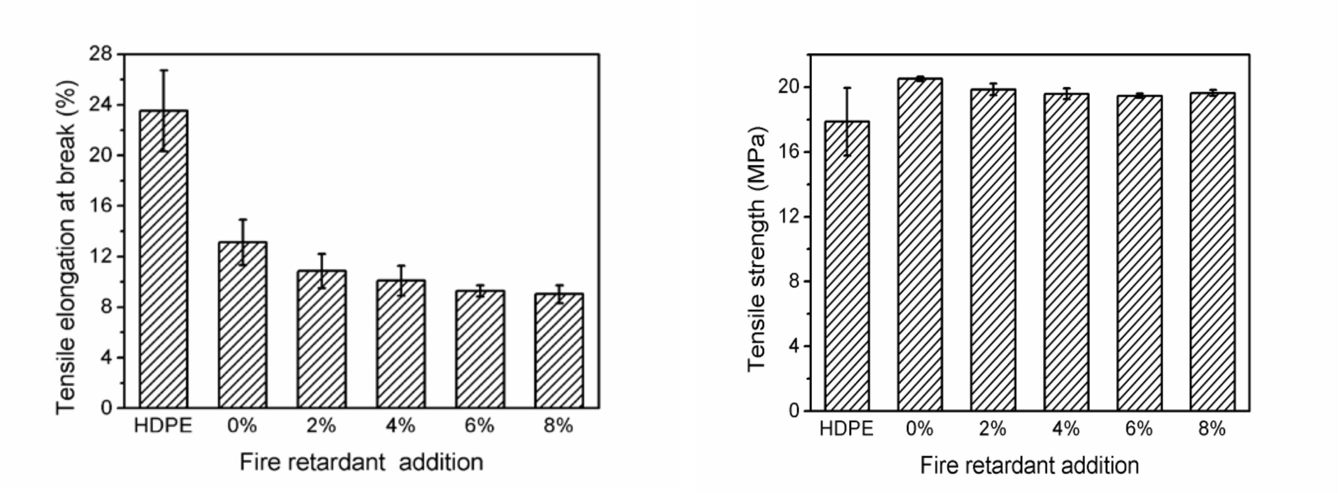
(a) (b)

(c) (d)

Fig. 1. Influence of fire retardant addition to wood flour-HDPE composites by cone calorimetry analysis (a) heat release rate (HRR), (b) total heat release (THR), (c) total smoke release (TSR), and (d) mass loss

Mechanical Properties

The tensile properties of the wood flour-HDPE composites are shown in Fig. 2. As usual in natural fiber reinforced with polymer composites, wood flour addition increased the tensile strength of the polymer composites by 14.8%, but it reduced the tensile elongation at break by 44.2%. Figure 2a also shows that the addition of fire retardant had no obvious effect on tensile strength of the wood flour-HDPE composite. However, with increasing fire retardant content from 0 to 10-wt%, the tensile elongation at break of wood flour-HDPE composites decreased gradually from 13.12 to 8.97%, as shown in Fig. 2b. As a rigid material, fire retardant has a higher stiffness than pure HDPE and wood flour. As a result, the HDPE composites with fire retardant became more rigid, creating regions of stress concentration, thus, decreasing the tensile elongation of composites.



(a) (b)

Fig. 2. Effects of fire retardant content on the tensile properties of the composites (a) tensile strength and (b) tensile elongation at break

Figure 3 shows the flexural properties of wood flour-HDPE composites. Addition fire retardant to wood flour-HDPE composites had a slightly higher flexural strength. As a rigid material, the fire retardant had a higher stiffness than HDPE and wood flour; thus the addition of fire retardant thus led to a higher flexural strength of the wood flour-HDPE composites.

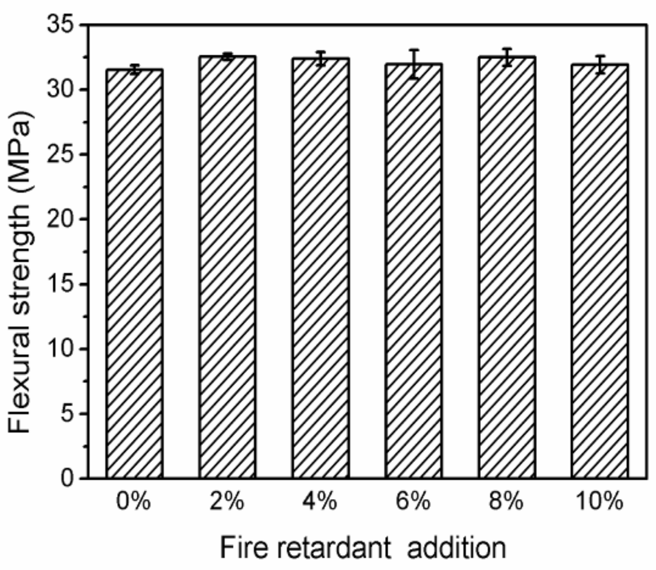


Fig. 3. Effects of fire retardant content on the flexural properties of the composites

The Charpy unnotched impact strength of the composites is presented in Fig. 4. To improve the flammability properties of the wood flour-HDPE composites, fire retardant was added to the system of wood flour-HDPE composites. However, it can be seen that the impact property of the composites decreased gradually from 1.42 to 0.82 kJ/m^2 as fire retardant content increased from 0 to 10-wt%. This is mainly due to energy dissipated by the fire retardant with more rigid. The impact properties reduction in APP treated wood-plastic composites has also been reported by other authors (Li and He 2004; Stark et al. 2010).

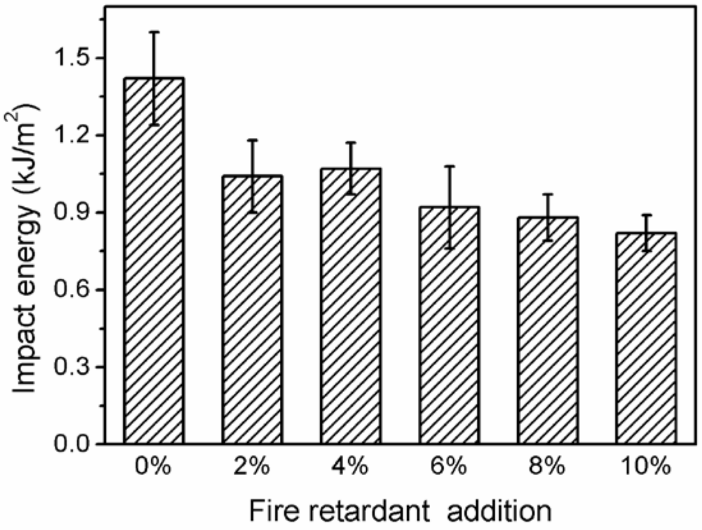


Fig. 4. Effects of fire retardant content on the impact properties of the composites

Scanning Electron Microscopy

The morphology of the fracture surface of the HDPE composites affected by fire retardant are presented in Fig. 5 (a, b, c, and d). From Fig. 5b, it can be seen that the fire retardant was very difficult to observe in composites with 2-wt% fire retardant. With increasing fire retardant up to 6-wt%, the fire retardant was uniformly diffused in wood flour-HDPE composites, as shown in Figs. 5c and 5d. Furthermore, it was difficult to observe the porosity structure in wood-HDPE composites without fire retardant, as shown in Fig. 5a.

With increasing fire retardant from 2 to 10-wt%, the porosity structure was obviously observed in composites, illustrated in Figs. 5b, 5c, and 5d. This is due to the fire retardant expanding enormously during the combustion reaction. Figure 5 also clearly shows the wood flour pullouts in the composites. This indicated that the addition of fire retardant led to a reduction in interfacial bonding between the HDPE and wood flour. Interfacial compatibility on fire retardant, wood flour, and polymer composites will be enhanced in a subsequent study.

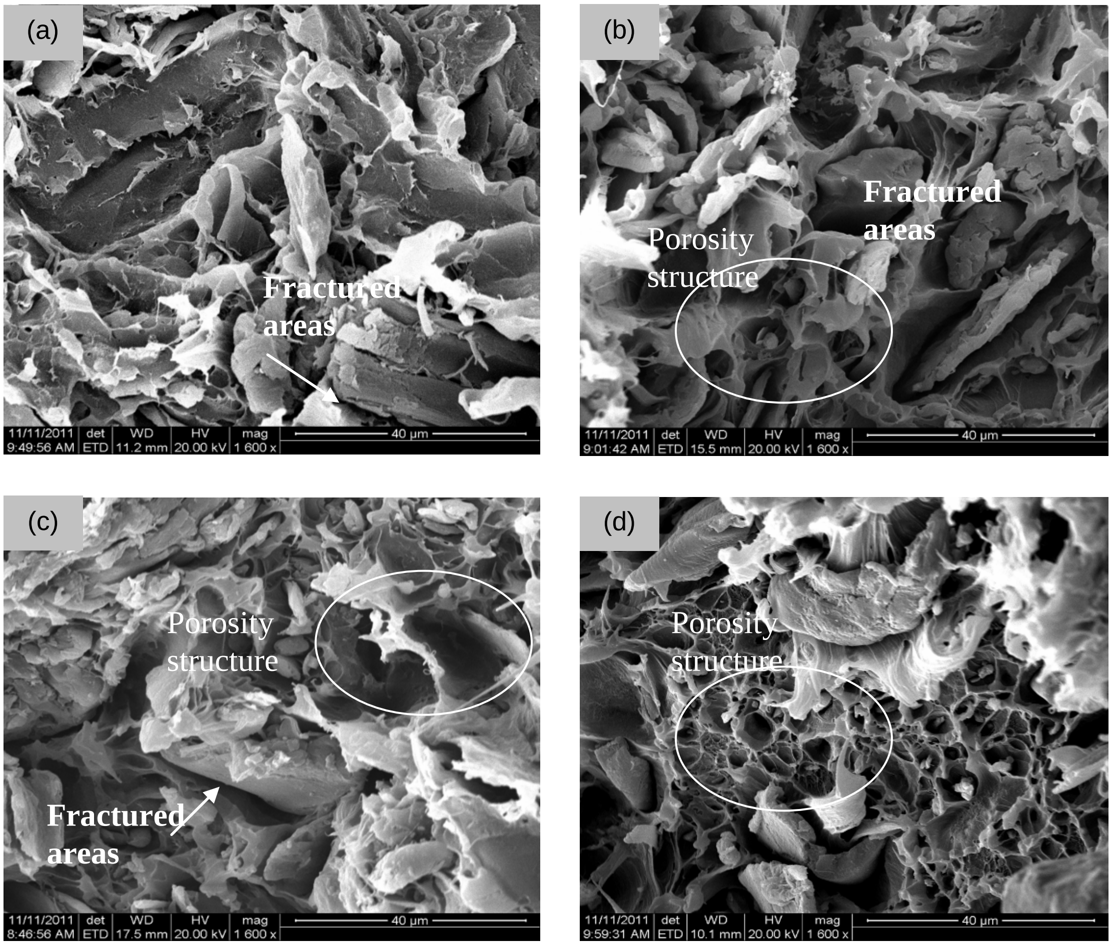


Fig. 5. SEM observations of the composites (a) P70W30, (b) P70W30F2, (c) P70W30F6, and (d) P70W30F10

CONCLUSIONS

The flammability behavior, mechanical properties, and morphology of wood flour-HDPE composites were investigated in this study. APP-based fire retardant had a positive effect on fire performance of wood flour-HDPE composites, and it could decrease the HRR and TSR of wood flour-HDPE composites. Moreover, the decrease of HRR mostly occurred with the concentration of fire retardant up to 4-wt%. With increasing fire retardant from 0 to 10-wt%, the tensile and flexural strength of wood flour-HDPE composites had no obvious effect. On the other hand, the tensile elongation at break and impact strength decreased significantly due to higher stiffness of the fire retardant. The SEM observation on the fracture surface of composites indicated that the fire retardant had a better dispersion in composites, and it could expand enormously in the course of a combustion reaction.

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