



Evaluation of various fire retardants for use in wood flour–polyethylene composites^{☆,☆☆}

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ABSTRACT

Wood–plastic composites represent a growing class of materials used by the residential construction industry and the furniture industry. For some applications in these industries, the fire performance of the material must be known, and in some cases improved. However, the fire performance of wood–plastic composites is not well understood, and there is little information regarding the effectiveness of various fire retardants in the public domain. We used oxygen index and cone calorimeter tests to characterize the fire performance of wood flour–polyethylene composites, and compared the results with unfilled polyethylene and solid wood. We then evaluated the effect of five additive-type fire retardants on fire performance. Generally, magnesium hydroxide and ammonium polyphosphate improved the fire performance of WPCs the most while a bromine-based fire retardant and zinc borate improved fire performance the least.

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1. Introduction

Wood–plastic composites (WPCs) represent an emerging class of materials that combines the favorable performance and cost attributes of both wood and plastics. Due to these attributes, forest-product companies see WPCs as a way to increase the value-added utilization of waste wood and wood of low commercial value. Plastic processors see wood as a readily available, relatively inexpensive filler that can lower resin costs, improve stiffness, increase profile extrusion rates, and act as an environmentally friendly way to decrease the use of petroleum-based plastics [1].

Currently several commercial WPCs are manufactured for the residential construction industry, primarily as lumber for decking and railing systems. WPCs are resistant to moisture, insects, decay, and warping when compared with traditional pressure-treated

lumber. WPCs are stiffer, exhibit less creep, and are more dimensionally stable than unfilled plastic lumber. In addition, WPCs offer a “wood” look and feel with minimum maintenance. Manufacturers are also introducing new applications for the furniture industry. Further expansion into the residential construction industry and development of applications for the furniture industry require an understanding of the fire performance of WPCs. For some applications it may be necessary to improve the fire performance, therefore a knowledge of the effect of fire retardants in WPCs is also critical.

The fire performance of plastics has been well characterized. The decomposition of burning plastics includes the production of combustible gases, non-combustible gases, liquids, solids (usually char), and entrained solid particles (smoke) [2]. Burning plastics may produce hazards such as the evolution of toxic gases, loss of physical integrity, and melting and dripping thereby providing other ignition sources. One strategy to improve the fire performance of plastics is to use additive-type fire retardants. Additive-type flame retardants are added to the plastic melt during processing and come in many forms, although most are particles or powders. Additive-type flame retardants can improve fire performance through the following mechanisms; 1) redirect decomposition and combustion reactions toward the evolution of non-combustible gases, or heavy gases that interfere with the interchange of combustion gases and air, 2) redirect the decomposition and

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combustion reactions toward reducing the heat of combustion, 3) maintain the physical integrity of the material, and 4) increase the specific heat or thermal conductivity [2].

1.1. Fire retardants

The compounds which have been found to be most effective in producing flame retardance are compounds containing bromine, chlorine, or phosphorous, or two or more of these elements. Other elements which have exhibited some flame retardant effects are antimony, boron, nitrogen, silicon, and zinc. These elements are often used with phosphorous or halogenated compounds.

Halogenated compounds based on chlorine and bromine are effective flame retardants. While there are environmental concerns regarding the use of these materials, bromine-based fire retardants are still widely used in polyolefins. Bromine-based fire retardants act in the condensed phase to redirect or terminate chemical reactions involved in combustion [3]. Heavy-bromine gases also protect the material from exposure to oxygen and heat [2]. A common bromine-based flame retardant is decabromodiphenyl oxide. Bromine-based flame retardants are practically always used with an antimony synergist, often antimony trioxide [3,4]. Antimony compounds alone do very little, but in combination with halogens form antimony trihalides. Antimony trihalides both scavenge free radicals and increase char formation [4].

Metal hydroxides are another common flame retardant. Metal hydroxides are typically aluminum-based or magnesium-based. Magnesium-based compounds are more suitable for polyolefins than aluminum-based compounds [4]. Both aluminum and magnesium are more effective as hydrated compounds. Decomposition of both aluminum hydroxide and magnesium hydroxide produces water vapor, which dilutes combustible gases. The heat required for dehydration also contributes to the fire retardant capabilities [2]. High loading levels of metal hydroxides increase the overall heat capacity of the material. Metal hydroxides perform as smoke reducers through the adsorption of carbon materials.

Boron-based flame retardants are generally char producers. The presence of boron can redirect decomposition to increase the production of carbon rather than carbon monoxide or carbon dioxide. By creating a surface layer of char, boron helps block oxygen from the surface and slows the escape of gases [2]. Boron can additionally work along with zinc in zinc borate compounds to reduce smoke production. Similar to metal hydroxides, most zinc borate compounds are used as hydrates. However, water removed from zinc borate during combustion does not change the chemical makeup of the compound [4]. The heat required for dehydration also contributes to fire retardant capability [4].

Phosphorous compounds redirect decomposition reactions in favor of reactions yielding carbon over carbon monoxide or carbon dioxide. The result is formation of a protective surface layer of char which inhibits access to oxygen [5]. It has been found that phosphorous does not increase char in polyolefins unless there is another char forming additive present, typically a nitrogen containing compounds [4]. Melamine is sometimes compounded with phosphates to achieve a phosphorous–nitrogen synergism. Melamine assists flame retardance in several ways while decomposing. It creates endothermic reactions and scavenges free radicals. Decomposition produces nitrogen and ammonia, which dilutes fuel gases. Melamine aids in char formation. Ammonium polyphosphate is another compound that takes advantage of the phosphorous–nitrogen synergism. Ammonium polyphosphate is known to intumesce [5]. In a heated environment, an intumescent material will foam, creating a barrier which blocks heat and oxygen from the flammable surface, improving charring. Ammonium polyphosphate also lowers smoke production, inhibits smoldering,

and helps resist flame migration [5]. However, ammonium polyphosphate is water soluble, so it may not be suitable for products exposed to exterior environments [5].

1.2. Fire performance of WPCs

The limited number of studies available on fire performance of WPCs indicates a need for a comprehensive investigation into the matter. Several studies have been conducted on commercial WPCs. Malvar et al. [6], evaluated several commercial WPCs, unfilled plastic lumber, and solid wood lumber for suitability as construction materials. Although they concluded that all evaluated WPCs were acceptable for building construction based on fire performance tests, there were some apparent differences in flame ignition temperatures. The lowest flame ignition temperature was found for solid wood, followed by WPCs and finally solid plastic lumber. Based on ignition temperature, the unfilled plastic performed better than WPCs, and solid wood, respectively.

White et al. [7] determined heat release rates for a variety of decking products including solid wood species, commercial and laboratory WPCs, and unfilled plastic. They reported the highest peak heat release rate for unfilled plastic, followed by WPCs and solid wood, respectively. Based on heat release rate, the fire performance of WPCs is better than unfilled plastic, but worse than solid wood [7]. This is in direct contrast with rating fire performance based on flame ignition temperature [6].

Heat release rate tests conducted on over 60 commercial lumber formulations showed a wide range of performance, but no information was given regarding specific formulations or geometries of the WPCs [8]. Although this study gives insight into the variability of fire performance of commercial WPCs, it does not add to the understanding of how formulation impacts fire performance. In general, fire performance tests conducted on commercial WPCs typically do not report the proprietary composition. The type of plastic matrix used and wood content may be known, but the additive type and content is not. Because commercial WPCs are used in building applications where fire performance standards must be met, and heat release rate data shows a wide range of performance, it can be assumed that flame retardants have been used in some commercial WPCs. However, this information is not in the public domain.

Studies conducted on manufactured WPCs where fire retardant type and concentration are known are limited. Halogenated compounds based on bromine, used in combination with antimony oxide, have been proven effective at improving the oxygen index of WPCs [9]. The reported effectiveness of metal hydroxides in WPCs has been mixed. Sain et al. [10] reported an improvement in oxygen index with the incorporation of magnesium hydroxide while Abu Bakar et al. [11] reported no positive effect on fire retardancy with the addition of magnesium hydroxide. Aluminum hydroxide has been shown to decrease WPC burning speed [12]. Boron-based compounds in the form of zinc borate have been studied primarily as a partial substitution for other fire retardants. Sain et al. [10] found that a partial replacement of magnesium hydroxide with zinc borate decreased oxygen index, lowering fire performance. Shen and Olson [9] found that partial substitution of a bromine-based fire retardant with zinc borate resulted in an increase in fire performance, while partial substitution of a phosphorous-based compound with zinc borate decreased WPC fire performance. Most research investigating fire retardants for WPCs has focused on phosphorous-based compounds. Comparisons between ammonium polyphosphate and melamine phosphate showed that ammonium polyphosphate was more effective at increasing oxygen index of WPCs [13]. Others have also reported positive effects of fire retardancy with use of ammonium polyphosphate [9,11].

Studies evaluating fire retardants for WPCs have shown that fire performance can be improved. However, it is impossible to compare various classes of fire retardants because the studies evaluated WPCs with different matrix materials and fire retardant contents using a range of fire performance tests. The main goal of this research project was to create a baseline of information reporting fire performance of WPCs and the effectiveness of additive-type fire retardants. Specific objectives included characterizing the oxygen index and heat release rate of wood–polyethylene composites and evaluating various classes of fire retardants for use in wood–polyethylene composites.

2. Experimental methods

2.1. Materials and manufacturing method

The base WPCs investigated consisted primarily of polyethylene (PE) and wood flour (WF). The PE had a 5-melt flow index and was purchased from ExxonMobil (HD 6605.70, Houston, TX). American Wood Fibers supplied 40-mesh, mixed pine WF (AWF 4020, Schofield, WI). To maintain good composite surface characteristics, a lubricant was added to each composite. Struktol Company of America supplied the lubricant (TPW 113, Stow, OH). In addition, five fire retardant systems were investigated:

- 1) Decabromodiphenyl oxide (Saytex 102E, Albemarle Corporation, Baton Rouge, LA) and antimony trioxide (BrightSun HB, China Antimony Chemicals Co., Ltd., Guangxi, China).
- 2) Magnesium hydroxide (Magnifin H-10, Albemarle Corporation, Baton Rouge, LA).
- 3) Zinc borate (FireBrake ZB, Rio Tinto Minerals, Valencia, CA).
- 4) Melamine phosphate (Melapur MP, Ciba Specialty Chemicals, Tarrytown, NY).
- 5) Ammonium polyphosphate (Exolit AP 422, Clariant Corporation, Charlotte, NC).

The formulations examined are shown in Table 1. Composites without fire retardants had either 50% or 60% by weight WF. Composites with fire retardants incorporated 50% WF and 10% of the fire retardant system. This allowed composites to be compared based on WF content (50%) or PE content (35%). Unfilled PE samples were also manufactured.

A 32-mm Davis Standard (Pawcatuck, CT) twin-screw co-rotating extruder combined with a Schenck AccuRate (Whitewater, WI) loss-in-weight feeder system was used for all compounding. The barrel of the extruder had 10 separate zones, with zones 4 and 9 vented to the atmosphere. The screw had a 36:1 L/D ratio consisting of primarily of conveying elements, with kneading and mixing elements incorporated into the screw before the vents to build up pressure and disperse and mix the components. The

extruder was outfitted with a strand die; the strand extrudate was cooled in a water slide and pelletized. The composites were compounded in two steps. In the first step, PE was compounded with or without fire retardant. This was to ensure thorough mixing of the fire retardant in the PE. The melt temperature ranged from 192 to 201 °C while the melt pressure ranged from 3.6 to 4.5 MPa. Prior to the second compounding step, WF was dried for 24 h at 105 °C. The dried WF was then compounded with lubricant and PE with or without fire retardant as shown in Table 1. During the second compounding step the melt temperature ranged from 188 to 199 °C while the melt pressure ranged from 4.2 to 7.0 MPa.

To form test samples for evaluating mechanical properties and oxygen index, compounded pellets were dried at 105 °C for at least 24 h just prior to injection molding into flexural bar test samples. The composites were injection molded using a 33-ton Cincinnati Milacron (Batavia, Ohio) injection molder. The mold nozzle temperature was 188 °C. The ASTM mold cavity used for the flexural samples was 12.7 mm by 3.2 mm by 127 mm [15].

To form composite boards for cone calorimeter testing, the compounded pellets were dried at 105 °C for at least 24 h before being processed into boards using a Davis Standard 89-mm single-screw extruder (Pawcatuck, CT). The melt temperature ranged between 167 and 174 °C. The extrudate was formed using a 12.7 mm × 127 mm (½" × 5") radius–edge profile die.

2.2. Fire performance tests

We determined oxygen index according to ASTM D 2863 using procedure A [16]. The oxygen index (OI) and corresponding estimated standard deviation were calculated according to the standard. Sample dimensions were as injection molded, a nominal 12.7 mm by 3.2 mm by 127 mm.

Cone calorimetry was performed on an Atlas Cone 2 Combustion Analysis System (Atlas Electrical Devices, Chicago, IL) according to ASTM E 1354 [17]. WPC samples were cut from the extruded boards to a size of 100 mm × 100 mm. The sample thickness was as extruded, at 12.7 mm. Samples were exposed in the horizontal orientation with the conical radiant electric heater located 25 mm above the specimen and the retainer frame (without the wire grid) over the test specimen. The sides and bottom of the samples were wrapped in aluminum foil. Each sample rested on an insulatory fiber blanket to keep it apart from the holder during the test. A spark igniter started the burning process and the length of time required to create a steady flame was recorded. Three replicate samples were tested at a heat flux level of 50 kW/m². The exhaust system flow rate was 0.024 m³/s. For PE samples, data collection for the first replicate ended when it was visually observed that there was very little material in the foil wrapper. Due to a high heat release rate, data collection for the remaining two PE replicates was stopped early, but not before 300 s after specimen ignition. Data collection for WPCs was stopped once the mass loss rate dropped below 1.5 g/m² s. The WPCs ceased burning once the heat from the cone was removed. For reference, pine boards cut to 100 mm × 100 mm by 12.7 mm were also subjected to cone calorimetry.

The primary result from the cone calorimeter test is a heat release rate (HRR) versus time curve. HRR is defined as the heat evolved from the specimen per unit time, and is determined by the oxygen consumed during burning [17]. Ignitability was determined by observing the time for sustained ignition of the specimen, and is reported as ignition time (IT). For reporting purposes, the heat release curve was reduced to single numbers via the recorded initial peak HRR and calculated averages of the HRR over a set time (60 s, 300 s, and over the test duration) after ignition of the specimen was observed. Total heat release (THR), i.e., the cumulative heat release over the duration of the test, average mass loss rate

Table 1
Formulations of WPCs manufactured with fire retardants.

Code	Composition based on weight (%)								
	PE	WF	BR	AT	MH	ZB	MP	AP	Lub
PE	100								
WF-50	45	50							5
WF-60	35	60							5
WF-BR	35	50	7.5	2.5					5
WF-MH	35	50			10				5
WF-ZB	35	50				10			5
WF-MP	35	50					10		5
WF-AP	35	50						10	5

PE = polyethylene, WF = wood flour, BR = decabromodiphenyl oxide, AT = antimony trioxide, MH = magnesium hydroxide, ZB = zinc borate, MP = melamine phosphate, AP = ammonium polyphosphate, Lub = lubricant.

(MLR), and average effective heat of combustion (EHO) for the test duration were also calculated according to ASTM D 1354 [17].

2.3. Mechanical properties

Flexural tests were carried out according to ASTM D 790 [15] on an MTS 810 Material Test System (MTS Systems Corp., Eden Prairie, Minnesota) with the exception that samples were oven dried at 105 °C for 24 h before testing rather than conditioned at 23 °C and 50% relative humidity for 40 h as the standard calls for. This is because WPCs take much longer to equilibrate than plastics. Testing samples oven-dry insures consistent moisture content for WPCs. A three-point loading system was utilized with a crosshead speed of 1.3 mm/min, which corresponds with an outer fiber strain rate of 0.01 mm/mm/min. Five replicate specimens were tested for each formulation. Flexural modulus of elasticity (MOE) and strength were calculated according to ASTM D 790 [15].

2.4. Statistics

Each bar in Fig. 2 and Figs. 5–11 represents the mean of that data set and error bars represent one standard deviation. To determine significant differences between compared means, two-sample *t* tests were carried out at $\alpha = 0.05$. Tests for significance were two-tailed and assumed normal distribution and equal population variances. Letters above the bars in each of these figures denotes significance. If the letters are the same, the hypothesis that the difference between means is zero was accepted. Conversely, different letters denote that the difference between means is not zero, i.e., the differences are statistically significant.

3. Results and discussion

The primary constituents of the WPCs we investigated, PE and wood, have different reported thermal properties (Table 2). Compared with wood, PE has a higher specific heat, defined as the amount of heat energy required to raise the temperature of the unit mass by one unit of temperature. However, the thermal conductivity, i.e., the rate at which heat flows through a given thickness of material under a given heat differential, is higher for PE than wood. Heating value refers to the production of heat per unit mass during combustion. The high heating value of PE compared with wood indicates that the combustion of PE produces more energy in the form of heat for a given mass than wood. Because WPCs are composite materials, we expect their fire performance to fall somewhere between that of PE and wood.

Two tests common for characterizing fire performance of plastic materials include the oxygen index (OI) test and cone calorimetry. We chose these tests to evaluate the fire performance of WPCs. The OI test is used to determine the lowest concentration of oxygen at which a material will maintain combustion in a flowing mixture of oxygen and nitrogen. The test does not predict how a material will perform in a fire, but is a good method for comparison between

Table 2
Reported thermal properties of unfilled polyethylene and solid wood.

Material	Specific heat (kJ/kg K)	Thermal conductivity (W/m K)	Heating value (MJ/kg)
PE	2.30 ^a	0.33–0.52 ^a	46.6 ^a
Wood	1.2 ^{b,c}	0.10 ^{b,d}	20.5 ^a

^a [2].

^b [19].

^c Oven-dry, at 290 K.

^d Oven-dry, ponderosa pine.

Table 3

Oxygen index results for polyethylene, 50% and 60% wood flour–polyethylene composites, and solid pine.

	Oxygen index ^a
PE	19.3 (0.2)
WF-50	19.7 (0.1)
WF-60	20.2 (0.2)
Pine	23.9 ^b (0.1)

^a Reported values and estimated standard deviations in parentheses determined using ASTM D 2863 [16].

^b Grain parallel to the long direction of the sample.

materials. A higher OI suggests better fire performance. Cone calorimetry is a test method that exposes a sample to a specific radiant flux and measures heat release rate, i.e., the heat evolved from the specimen per unit of time. Heat evolved from a material can contribute to the temperature of the environment and the rate of fire spread. Therefore, it is desirable for a material to have a lower HRR to decrease the contribution to a fire.

3.1. Fire performance of WPCs

Oxygen index (OI) results for PE, WPCs, and solid pine are reported in Table 3. The OI of wood was higher than that of PE. This suggests that wood may be easier to extinguish in a fire than PE due to the higher concentration of oxygen required to sustain burning. The OI of WPCs was higher than PE, but lower than wood. Incorporating more wood into the composite (WF-60 versus WF-50) resulted in an improved OI.

Representative HRR versus time curves for PE and WPCs (WF-50 and WF-60) are shown in Fig. 1. For comparison, a representative HRR curve for solid pine is included. Examination of the HRR versus time curve shows that the HRR of PE started increasing later than the HRR of pine. However, the HRR of PE continued to increase until the material was consumed, while the HRR of pine reached a peak early during the test duration, then reached a second peak later in the test. The peak HRR of PE was higher than the peak HRR for solid pine. The HRR of WPCs reached a peak early in the test, and then gradually decreased throughout the test. The peak HRR for WPCs fell between that of PE and solid pine.

Cone calorimeter results for PE, WPCs (WF-50 and WF-60), and solid pine is shown in Table 4. A material performs best in a fire with a higher IT and lower HRR. Comparing the fire performance of PE with pine shows that although IT of PE is higher than pine, the calculated HRRs, THR, MLR, and EHO are also all higher for PE than pine. The results suggest that although it takes longer for PE to

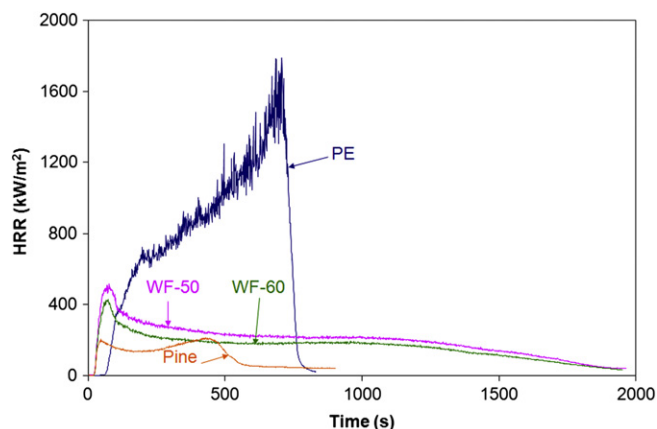


Fig. 1. Representative HRR curves for polyethylene, 50% and 60% wood flour–polyethylene composites, and solid pine.

Table 4
Cone calorimeter results for polyethylene, 50% and 60% wood flour–polyethylene composites, and solid pine.^a

	IT ^b (s)	Peak HRR ^c (kW/m ²)	Average HRR ^c			THR ^d (MJ/m ²)	MLR ^e (g/s m ²)	EHOC ^f (MJ/kg)
			60 s (kW/m ²)	300 s (kW/m ²)	Total test (kW/m ²)			
PE	82.2 (9.5)	1790 ^g	284 (21)	635 (32)	893 ^g	609 ^g	22.7 ^g	43.6 ^g
WF-50	24.5 (0.3)	505 (18)	369 (13)	326 (7)	207 (7)	373 (6)	7.8 (0.2)	30.0 (0.6)
WF-60	24.9 (0.3)	437 (15)	315 (3)	260 (1)	167 (7)	317 (10)	7.5 (0.1)	25.8 (0.5)
Pine	22.2 (2.1)	209 ^h (2)	171 (11)	157 (8)	139 (7)	94 (6)	13.0 (0.2)	13.7 (0.2)

^a Reported values represent means with standard deviations in parentheses based on three replicates.

^b Ignition time (IT).

^c Heat release rate (HRR).

^d Total heat release (THR).

^e Average mass loss rate (MLR).

^f Average effective heat of combustion (EHOC).

^g Data for one sample only.

^h First peak.

ignite compared with wood, once ignition is underway PE releases more heat and combustion consumes material faster than wood. The reported thermal properties support this (Table 2). The higher specific heat of PE compared with wood means that more heat is required to start combustion of PE, but once combustion is underway the higher thermal conductivity and heating value of PE translates to higher HRRs, THR, MLR, and EHOC.

Generally, the fire performance based on cone calorimetry of WPCs fell between that of PE and solid wood (Table 4). The IT of WPCs was similar to wood and lower than PE. The peak HRR of WPCs was lower than PE and higher than solid wood. A comparison between the two WPCs showed that the WPC with more wood (60% versus 50%) had a lower peak HRR. This is consistent with an earlier study which reported a decrease in HRR with increasing wood content [18]. Borysiak et al. [14] also found that wood–polypropylene composites had earlier ignition times and lower peak HRR compared with unfilled polypropylene samples. It is interesting that 60 s after ignition, the average HRR was higher for WPCs than for solid pine or PE. However, 300 s after ignition and for the duration of the test, the average HRR of WPCs was lower than the average HRR of PE and higher than the average HRR of pine. This was because WPCs reached their peak HRR during the first 60 s after ignition, while the HRR of PE increased throughout the test duration. The THR and EHOC of WPCs were also lower than PE, but higher than solid wood. However, the gradual decrease in HRR of WPCs compared with PE or pine results in a lower MLR.

Both OI results and cone calorimetry results suggest that fire performance of WPCs is better than PE but not as good as solid

wood. This is consistent with better fire performance being obtained when PE is displaced with wood in a composite. For example, adding 60% wood by weight to PE decreased peak HRR of PE by 75% and THR by 48%.

3.2. Effect of fire retardants

Additive-type fire retardants were incorporated into WPCs to improve fire performance. Because the thermal conductivity and heating value of PE had a large impact on fire performance, we chose to compare results between WPCs with the same PE content. In our case, WF-60 and WPCs containing fire retardants all had a 35% PE content. In this manner incorporating fire retardants into the WPCs can be thought of as a partial replacement of wood with another filler.

OI and cone calorimetry were also used to evaluate the performance of fire retardants in WPCs. Each of the fire retardant systems had a positive effect on OI (Fig. 2). Compared with WF-60, the most effective was AP, which increased OI by 29%.

Representative HRR versus time curves for WPCs with and without fire retardants are shown in Fig. 3. It is easily seen that all fire retardants lower HRR of WPCs. Overall AP decreased the HRR the most, but also led to a smaller HRR for a longer duration. An expansion of the HRR peak (Fig. 4) shows a broad range of peak HRRs. Comparing WPCs containing fire retardants, WPCs containing BR had the highest peak HRR while WPCs containing MH had the lowest.

Incorporating fire retardants in WPCs had a mixed effect on ignition time (Fig. 5). Fire retardants that significantly improved IT compared with WF-60 (i.e., increased it) include BR and MH. AP

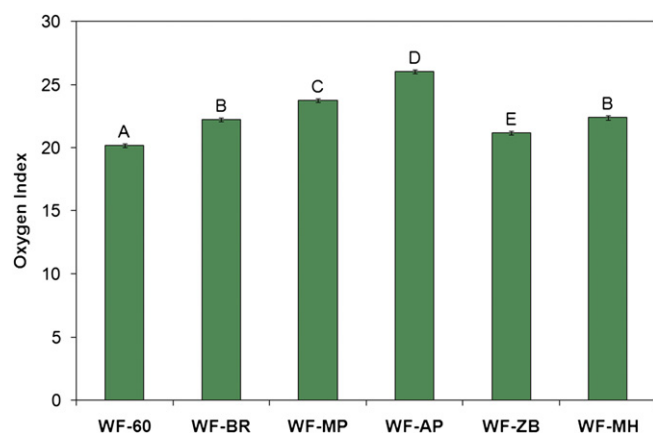


Fig. 2. Oxygen index for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

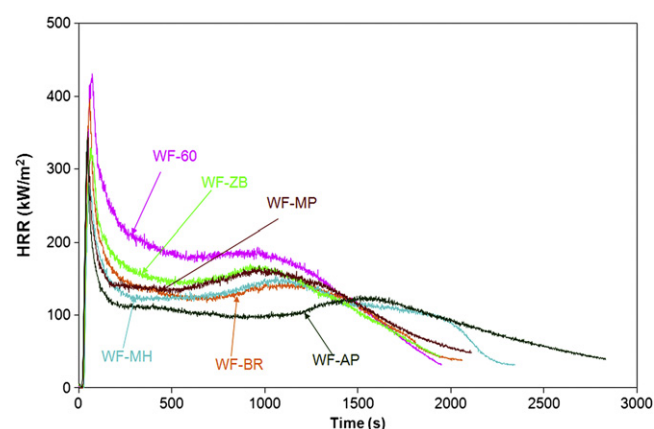


Fig. 3. Representative HRR curves for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

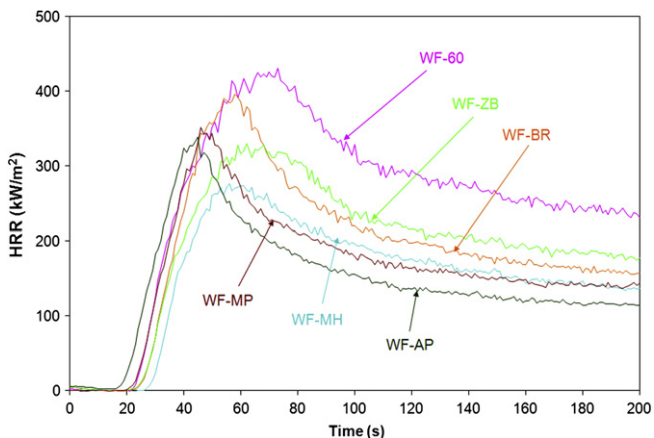


Fig. 4. Expansion of the peak of representative HRR curves for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

significantly decreased the ignition time. Compared with WF-60, MH increased IT by 24% and AP decreased IT by 12%.

Fig. 6 summarizes peak HRR as well as HRR averaged over 60 s, 300 s, and the entire test duration once ignition was observed. All fire retardants significantly improved the peak HRR and average HRRs of WPCs. Compared with WF-60, peak HRR of WPCs decreased between 11% and 35% when fire retardants were added. WPCs containing MH performed the best while WPCs containing the BR performed the worst. Fire retardants also influenced the average HRR over the total test duration. Compared with WF-60, the average HRR over the test duration decreased between 19% and 39% when fire retardants were added. For average HRR, AP improved the fire performance of WPCs the most. Although ZB improved the fire performance of WPCs the least, the performance was not significantly different from MP and BR.

Each fire retardant system significantly lowered THR, ranging between 15% and 24% improvement (Fig. 7). Although BR improved THR the most, the performance was not statistically different from WPCs containing MP. While MH improved THR the least, the performance was not statistically different from WPCs containing AP.

Each fire retardant system also significantly lowered MLR, but the magnitude of the improvement varied greatly (Fig. 8). Compared with WF-60, fire retardants lowered the MLR between

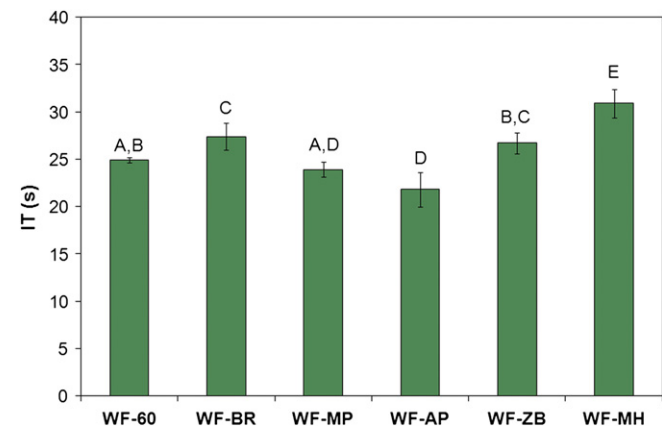


Fig. 5. Observed ignition time (IT) for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

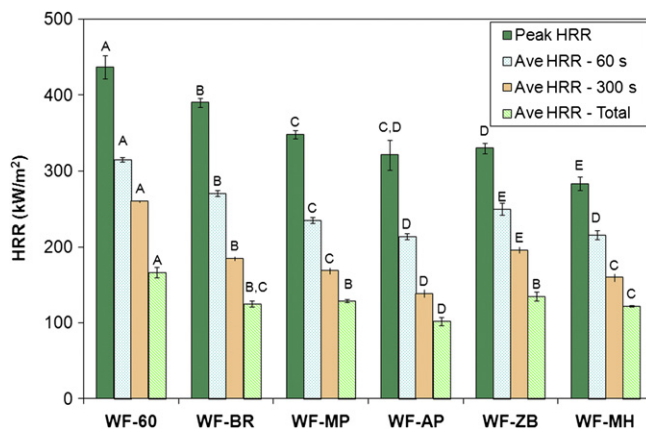


Fig. 6. Calculated heat release rates (HRRs) for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

11% and 43%. The most improvement was shown when AP was added, while adding BR improved MLR the least.

The only fire retardant to significantly change EHOc was BR (Fig. 9). Compared with WF-60, the WPC containing BR significantly decreased EHOc by 17%. The remaining fire retardants did not significantly change EHOc.

The mechanical properties of PE and WPCs (WF-50 and WF-60) are reported in Table 5.

For comparison, mechanical properties of solid pine with the grain direction parallel to the long dimension of the sample are also reported. Adding WF to PE increased the MOE. Adding 50% WF to PE also increased the strength, but adding 60% WF decreased the strength. The flexural MOE and strength of the WPCs were much lower than that of solid pine.

The effect of fire retardants on composite mechanical properties is shown in Figs. 10 and 11. Similar to fire performance comparisons made between WPC formulations, we chose to compare the properties of WPCs with fire retardants with WF-60. Compared with WF-60, incorporation of ZB increased the MOE 14%, while incorporation of AP decreased the MOE 24% (Fig. 10). The remaining fire retardants did not significantly affect MOE. Compared with WF-60 all fire retardants significantly changed WPC strength; BR, ZB, and MH increased strength while MP and AP decreased strength (Fig. 11). Similar to the effects on MOE, ZB provided the greatest strength improvement (21%) while AP decreased the strength the most (20%).

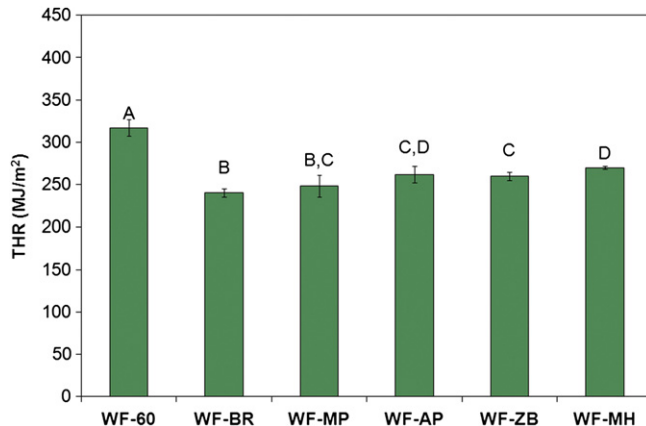


Fig. 7. Calculated total heat release (THR) for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

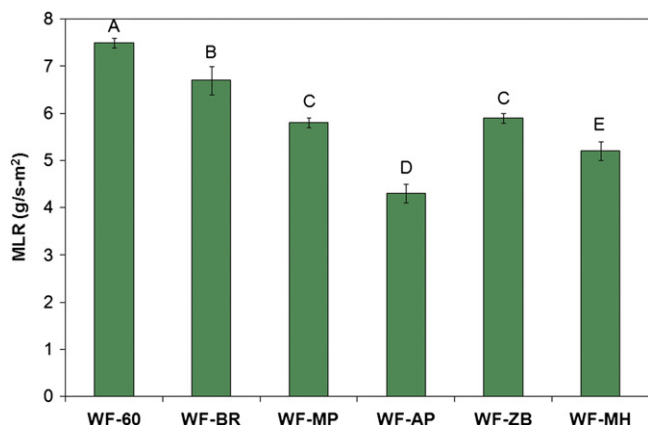


Fig. 8. Calculated average mass loss rate (MLR) for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

4. Summary

There is potential for WPCs to expand into new and existing applications in the residential construction and furniture industries. However, incomplete knowledge regarding the fire performance of WPCs and the effectiveness of fire retardants limits this expansion. In this study, we used oxygen index tests and cone calorimetry to characterize the fire performance of wood flour–polyethylene composites compared with unfilled PE and solid wood. We also evaluated the effect of five additive-type fire retardants systems on fire performance.

The oxygen index of wood–polyethylene composites was reported to be higher than PE and lower than wood. The HRR of wood–polyethylene was generally lower than PE and higher than pine. The peak and average HRR for the test duration of WPCs was closer to wood than PE. This combination of results suggests that WPCs exhibit improved fire performance over PE, but perform worse than solid wood. Compared with PE, the ignition time of WPCs was shorter and 60 s after ignition the average HRR was higher. As the tests continued, the HRR of PE increased rapidly until the material was consumed, while the HRR of WPCs reached an initial peak and then decreased slowly. Therefore the fire performance of WPCs is better than unfilled PE, and worse than solid wood. This is largely due to the lower thermal conductivity and heating value of wood compared with PE.

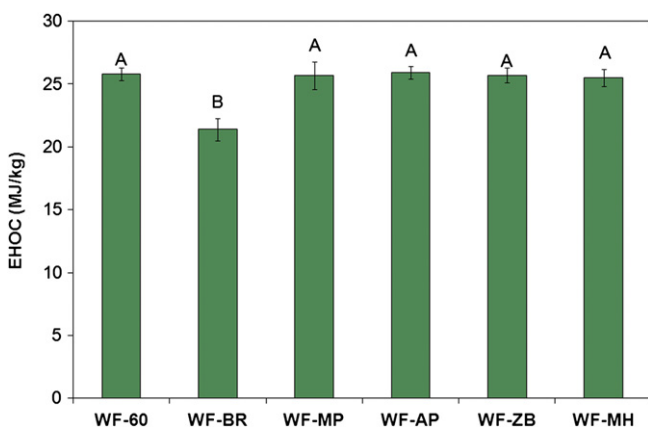


Fig. 9. Calculated average effective heat of combustion (EHOC) for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

Table 5

Mechanical properties of polyethylene, 50% and 60% wood flour–polyethylene composites, and solid pine.

	MOE ^b (GPa)	Strength ^b (MPa)
PE	1.34 (0.02)	32.1 (0.1)
WF-50	4.42 (0.15)	35.9 (0.5)
WF-60	4.55 (0.21)	29.5 (0.7)
Pine ^a	5.82 (0.57)	119.9 (6.9)

^a Grain parallel to the long dimension of the sample.

^b Reported values represent means with standard deviations based on five replicates.

All fire retardant systems examined improved the OI and HRR of WPCs. Some fire retardant systems improved ignition time while others did not. The following summarizes the performance of the fire retardants studied.

- The bromine-based fire retardant generally performed the worst on the cone calorimeter tests. Improvements in peak HRR, average HRR after 60 s, average HRR for the test duration, MLR, and EHOc were all lowest for the bromine-based fire retardant. However, the bromine-based fire retardant did not change MOE and improved the strength.
- Magnesium hydroxide increased ignition time the most. During the initial stages of cone calorimetry, magnesium hydroxide performed well. The best improvements in peak HRR and average HRR after 60 s occurred with the addition of magnesium hydroxide. However, the THR was among the worst.
- Overall, zinc borate did not perform as well as the other fire retardants. The worst oxygen index was observed when zinc borate was used. At later times during cone calorimeter tests, the average HRR after 300 s and average HRR for the total test were the worst. However, the best mechanical properties were observed with zinc borate.
- Although melamine phosphate provided improved fire performance, it was generally neither the best nor worst performer in oxygen index tests and cone calorimeter tests.
- Ammonium polyphosphate generally performed well as a fire retardant. The best oxygen index, average HRR after 60 s, 300 s, and over the test duration, and mass loss rate were reported when ammonium polyphosphate was used. However, WPCs containing ammonium polyphosphate had the shortest ignition time, and the highest total heat release. Also, ammonium polyphosphate had a negative effect on mechanical properties.

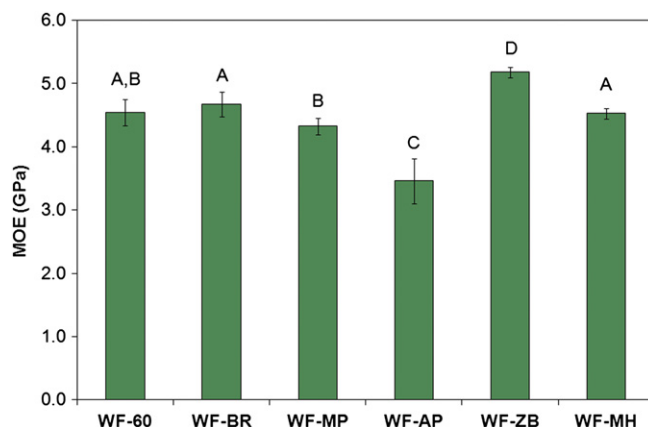


Fig. 10. Flexural MOE for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

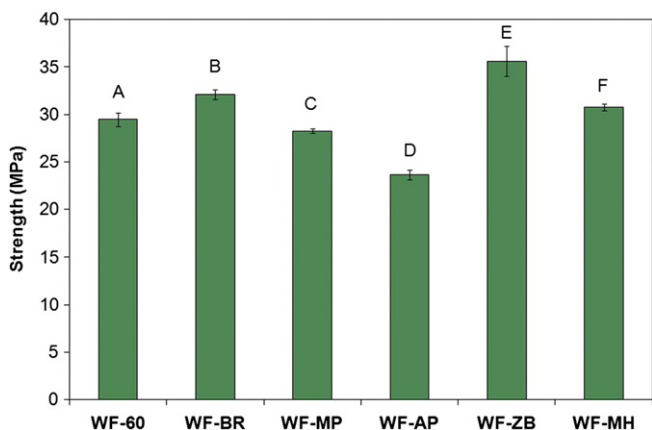


Fig. 11. Flexural strength for 60% wood flour–polyethylene composites and for 50% wood flour–polyethylene composites with 10% fire retardant.

This study provides a baseline of fire performance of WPCs based on oxygen index and cone calorimetry tests. It also demonstrates the changes in fire performance that can be obtained when various additive-type fire retardants are incorporated into WPCs. Based on these results magnesium hydroxide and ammonium polyphosphate were identified as the most effective fire retardants for WPCs, with a note that ammonium polyphosphate may negatively impact mechanical properties.

The work presented here was meant to gather data with consistent formulations, materials, and methodologies. The complex nature of flame retardance, i.e., each fire retardant is effective via several mechanisms, does not allow us to easily draw conclusions regarding mechanisms of flame retardance for WPCs. For example, the decomposition of magnesium hydroxide produces water vapor which contributes to fire retardant capabilities. However, zinc borate compounds also produce water vapor and did not perform well. Ammonium polyphosphate intumesces and aids in char production, but char producers such as bromine-based compounds and boron-based compounds did not perform well.

Although all fire retardants had a positive effect on fire performance of WPCs, it is interesting to note that the addition of wood flour alone into PE can dramatically improve the fire performance of PE. For example, incorporating 60% wood into PE lowered the peak HRR of PE by 76%. In comparison, incorporating 50% wood and 10% magnesium hydroxide (the combination that improved peak HRR the most) decreased the peak HRR of PE by 84%.

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