Colemanite: A Fire Retardant Candidate for Wood Plastic Composites

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The use of raw boron minerals (*i.e.* tincalconite, colemanite, and ulexite) was evaluated to increase the fire performance of wood plastic composites (WPCs) in comparison with commercially available fire retardants (FRs). Cone calorimetry and limited oxygen index tests were performed to evaluate the fire properties of WPC specimens. Artificial weathering and 3-point bending tests were also performed on the test specimens loaded with the highest loading level of FRs. The most important decrease in the heat release rate values was 42% and 40% in the magnesium hydroxide- and colemanite-added WPCs at a loading level of 15% (w/w), respectively. Incorporation of colemanite and ulexite into the WPCs increased the limited oxygen index levels by nearly 13% at the same loading level. An increase was observed in the peak heat release rate values in all of the WPC specimens after accelerated weathering. All of the FRs had statistically improved MOE values compared with the control WPC specimens. In particular, the incorporation of zinc borate and borax increased the MOE values by approximately 48% and 42%, respectively. Similar to the effect on the MOE values, zinc borate and borax improved the modulus of rupture the most (approximately 18%).

Keywords: WPC; Raw boron minerals; Cone calorimeter; Limited oxygen index; Artificial weathering

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INTRODUCTION

For a more efficient use of wood as a raw material, the combination of wood with other materials has gained importance. Various types of wood plastic composites (WPCs) have been introduced to the market. In WPCs, wood is used as a filler and an additive in a polymer matrix to improve thermal and mechanical properties of the matrix with cost efficiency. However, the current knowledge of several properties of WPCs is inadequate. For building materials, the fire performance of WPCs must comply with international norms and regulations. To enhance these characteristics, numerous studies are in progress to find suitable additives in the production of WPCs (Klyosov 2007; Terzi 2015).

Polyolefins are generally used as the polymer matrix for WPC products. Polyethylene and polypropylene are common polyolefins. The peak heat release rate and mass lose rate values of these polymers can reach high levels. The heat release rate (HRR) is the most important parameter in cone calorimetry tests for the assessment of the fire hazard. The incorporation of a flame retardant lowers the heat release rate (Babrauskas and Peacock 1992; Grexa and LUbke 2001; Mouritz and Gibson 2007; Hirschler 2015). The addition of wood-based fillers, such as wood flour, to polyolefins reduces the peak heat release and mass loss rates remarkably, but they can accelerate the ignition time compared with pure polyolefins depending on the specific heat and smoke production (Borysiak *et al.* 2006; Stark *et al.* 2010; Ayrilmis *et al.* 2012; Arao *et al.* 2014; Umemura *et al.* 2014; Mohamed and Hassabo 2015). To comply with international standards and regulations, numerous studies investigating the fire performance of WPCs are in progress. These studies incorporate fire retardants (FRs) into the WPC formulation at different manufacturing stages (Li and He 2004; Stark *et al.* 2010; Naumann *et al.* 2012; Arao *et al.* 2014), during production (mass treatment) or applied onto the surface of WPCs during the final stage of production (surface protection) (Mohamed and Hassabo 2015). FR-treated wood flour can be added to improve the fire performance of WPCs, but this application is rare due to the increased associated costs (Seefeldt and Braun 2012; Hämäläinen and Kärki 2014; Schirp and Su 2016).

Different types of FRs can be used as fillers in polymers. Halogenated and phosphohalogenated compounds are effective and common, but they potentially produce toxic gases during combustion (Garcia *et al.* 2009). Therefore, research has focused on halogen-free FRs because of environmental concerns. Inorganic boron minerals are active FR fillers that are more effective than inert fillers at reducing the flammability and smoke produced by polymer composites. Active fillers act as heat sinks and dilute the mass fraction of organic matrix material in a composite. Such fillers work in the condensed phase by decomposing at high temperatures through endothermic reactions. This gives the composite an ability to absorb a large amount of heat and a cooling effect that slows the thermal decomposition rate of the polymer matrix. The thermal decomposition reaction of the filler also results in a large amount of inert gases, such as water vapor and carbon dioxide. These inert gases then dilute the concentration of flammable volatiles (methane, ethane, *etc.*) and free radicals, which causes a reduction in the flame temperature and thermal decomposition rate of the material (Mouritz and Gibson 2007).

FR chemicals that are commonly used in WPCs are metal hydroxides such as magnesium hydroxide, aluminum hydroxide, boric acid, ammonium phosphate, ammonium borate, ammonium sulphate, ammonium chloride, zinc chloride, zinc borate, phosphoric acid, dicyanodiamide, sodium borate, and antimony oxide. Nano-scale new-generation chemicals, including nanotubes and nanoclay, are also used (Shen and Olson 2006; Guo *et al.* 2007; Klyosov 2007; Mouritz and Gibson 2007; Han *et al.* 2008; Fu *et al.* 2010; Stark *et al.* 2010; Min *et al.* 2013; Nemati *et al.* 2013; Cavdar *et al.* 2015; Mohamed and Hassabo 2015). These additives are used in powder form at 5% to 10% of the dry mass; for nano-scale chemicals this ratio is approximately 1% (Guo *et al.* 2007; Fu *et al.* 2010; Mohamed and Hassabo 2015). Unfortunately, these chemicals may adversely affect the mechanical properties of WPCs. Some researchers have reported that ammonium polyphosphate and magnesium hydroxide reduce the modulus of rupture (MOR) of WPC products (Stark *et al.* 2010; Ayrilmis *et al.* 2012).

The FR characteristics of boron compounds derived from boron minerals have long been known and used in the wood and wood-based material protection industry. Turkey has 72% of the global boron reserves based on the high B_2O_3 content. Boron minerals are also found in large deposits in South America and the USA. The most common boron ores in terms of reserves in Turkey are colemanite ($2CaO\cdot 3B_2O_3\cdot 5H_2O$) and tincal ($Na_2B_4O_7\cdot 10H_2O$). Sodium (Na), calcium (Ca), magnesium (Mg), and Na-Ca hydrate borates are alternate forms of each. Examples of alternate forms includes inyoite, meyerhofferite, and colemanite; borax, tincalconite, and kernite; probertite and ulexite; suanite and ascharite; gowerite and nobleite; and inderite and kurnakovite. High grade commercial colemanite (B_2O_3 content: 50.8 wt.%) is obtained from reserves in Turkey and is used to produce boric acid. Turkey also has ulexite, which is a boron mineral with a B_2O_3

content of up to 43%. However, ulexite is not as common as colemanite in Turkey (Kistler and Helvaci 1994; Birsoy and Özbaş 2012; Özdemir *et al.* 2014; Terzi 2015).

In this study, raw boron minerals (tincalconite, colemanite, and ulexite) were tested without any further chemical processing as additives in WPCs to determine the fire performance of the material. WPCs are increasingly used in residential construction and furniture manufacturing. The WPC industry can use the knowledge of fire properties to improve the fire performance of WPCs and expand into new markets, such as the building, furniture, and automotive industries. Inadequate knowledge of the fire performance of WPCs and the effectiveness of FRs restricts this growth (Stark *et al.* 2010). Tincalconite, colemanite, and ulexite, which are raw boron minerals with varying amounts of boron oxide (B_2O_3) in their chemical structures, were investigated because of high-reserves of such boron minerals in Turkey. Because WPCs are a heterogeneous composite consisting of wood fillers and additives in polymers, the use of raw boron minerals as additives is not expected to cause problems during processing. Thus, the use of raw boron minerals in various applications without the use advanced technologies for purification could be sustainable. Raw boron minerals can be used to produce FR compounds, such as those that have long been used in wood and wood-based composites. As reference chemicals, magnesium hydroxide and zinc borate, which are used commonly in WPCs as FRs, were evaluated in this study. Borax was also tested as a reference boron compound.

EXPERIMENTAL

Materials

Additives and chemicals used for the production of WPC deck boards were classified in three groups (raw boron minerals, commercial FR additives, and coupling agent) and are listed below. The thermal properties of the raw boron minerals and commercial FR additives were investigated with a thermogravimetric/differential thermal analyzer (Pyris Dimon, Perkin Elmer, Waltham, MA, USA) to determine the fire retardancy effect of the additives. The experiments were performed under a nitrogen atmosphere (99.999% purity, 200 mL/min), and heating from room temperature to 550 °C occurred at a 10 °C/min. The thermogravimetric and heat flow profiles are given in SUPF1.

Raw boron minerals (Eti Boron Corp., Balıkesir, Turkey) were milled and passed through a 60-mesh sieve before WPC production. The materials used were colemanite (C, $Ca_2B_6O_{11}\cdot 5H_2O$, boron content: 15.78%), tincalconite (T, $Na_2B_4O_7\cdot 5H_2O$, boron content: 15.16%), and ulexite (U, $NaCaB_5O_9\cdot 8H_2O$, boron content: 13.34%). The commercial FR additives borax (B, $Na_2B_4O_7\cdot 10H_2O$; boron content: 11.34%, Eti Boron Corp., Balıkesir, Turkey), magnesium hydroxide (M, $Mg(OH)_2$; BDH Chemicals Ltd., Poole, UK) and zinc borate (Z, $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$; boron content: 14.92%, Melos Corp., Sakarya, Turkey), were used as received. The coupling agent was ethylene acid copolymer (Fusabond∼ M603 resin, Dupont, Wilmington, DE, USA).

Methods

Production of the WPC deck boards

High-density polyethylene (HDPE) (Petilen YY S 0464, Petkim, İzmir, Turkey; density: 0.962 to 0.966 g/cm^3, melt mass-flow rate: 0.25 to 0.45 g/10 min (190 °C/2.16 kg)) was used in this study. The coupling agent was ethylene acid copolymer (Fusabond® M603 resin). Sixty-mesh wood flour derived from sawn timber (*Abies* spp.) waste was oven-dried at 103 ± 2 °C and used as filler for the commercial-scale manufacturing process.

The wood flour, HDPE pellets, coupling agent, and FR additives were compounded using a conical twin-screw extruder, according to Table 1. The barrel temperature of the extruder was approximately 180 °C. These compounds were used to extrude solid type WPC deck boards (25 × 140 × 2000 mm). These deck boards were used to prepare test specimens according to fire, mechanical, and artificial weathering test standards (ASTM D2565-99 2008; ASTM D618-08 2008; ASTM D790-10 2010; ASTM D2863-13 2013; ASTM E1354 2014). The moisture content of all specimens were below 1%.

Table 1. Composition and Formulation of the Wood Plastic Composite (WPC) Specimens

Specimen ID	HDPE (/o w/w)	Wood Flour (/o w/w)	FR Percentage (/o w/w)	Coupling Agent* (/o w/w)
Control WPC	49	50	-	1
M-5	44	50	5	1
M-10	39	50	10	1
M-15	34	50	15	1
Z-5	44	50	5	1
Z-10	39	50	10	1
Z-15	34	50	15	1
B-5	44	50	5	1
B-10	39	50	10	1
B-15	34	50	15	1
C-5	44	50	5	1
C-10	39	50	10	1
C-15	34	50	15	1
U-5	44	50	5	1
U-10	39	50	10	1
U-15	34	50	15	1
T-5	44	50	5	1
T-10	39	50	10	1
T-15	34	50	15	1

HDPE = high density polyethylene, M = magnesium hydroxide, U = ulexite, C = colemanite, B = borax (tincal), T = tincalconite, Z = zinc borate; *Ethylene acid copolymer

Cone calorimetry test

Cone calorimetry tests were performed with an Atlas Cone 2 Combustion Analysis System (Atlas Electrical Devices, Chicago, IL) according to ASTM E1354 (2014). WPC specimens (100 × 100 × 8 mm) were cut from the extruded deck boards. All specimens were conditioned in a humidity-controlled room at 23 °C and 50% relative humidity (RH) for at least four weeks prior to the tests. Three replicate specimens were tested at a heat flux level of 50 kW/m^2 to simulate a room fire (Mouritz and Gibson 2007). The HRR was defined as the heat evolved from the specimen per unit time, and was determined by the oxygen consumption during burning according to ASTM E1354 (2014). Ignitability was then determined by observing the time for sustained ignition (existence of flame on or over most of the specimen surface for periods of at least 4 s) of the specimen, and reported as the time to sustained ignition (TTI) (ASTM E1354 2014).

Limited oxygen index (LOI) test

The limited oxygen index (LOI), a parameter for evaluating the flame retardancy and flammability of polymeric materials, was tested on an oxygen index instrument (Custom Scientific Instruments Inc., NJ, USA) at room temperature according to ASTM

D2863-13 (2013). The LOI test is a bench-scale test developed in place of small-scale tests that were used to evaluate the flammability and ignition properties of combustion materials in previous years and which have reproducibility problems. The LOI value expresses the lowest volume concentration of oxygen that sustains candle-like burning of materials in mixing gases of nitrogen and oxygen for at least 3 min (Mouritz and Gibson 2007). Test specimens (4 × 10 × 100 mm) were cut from the extruded WPC deck boards. All specimens were conditioned in a humidity-controlled room at 23 °C and 50% RH for at least four weeks prior to performing the tests, according to ASTM D618-08 (2008). Ten replicate specimens were tested.

Because of possible inconsistencies in the up-and-down sequence of oxygen concentrations, the oxygen index (*OI*), expressed as a percentage by volume, was calculated from the following relationship,

$$OI = CF + k * d \tag{1}$$

where *CF* is the final value of the oxygen concentration (% vol. to one decimal place), *d* is the interval (% vol. to at least one decimal place) between the oxygen concentration levels used, and *k* is a factor determined from Table 3 as described in ASTM D2863-13 (2013).

3-point bending test

Flexural tests were carried out according to ASTM D790-10 (2010) on an MTS 810 Material Test System (MTS Systems Corp., Eden Prairie, MN) on control and FR-incorporated WPC specimens at a loading level of 15% (w/w). Test specimens (5 x 20 x 115 mm) were cut from the extruded WPC deck boards. All of the specimens were then conditioned in a humidity-controlled room at 23 °C and 50% RH for at least two weeks before the flexural tests. A 3-point loading system was operated with a crosshead speed of 1.3 mm/min, which corresponded to an outer fiber strain rate of 0.01 mm/mm/min. Five replicate specimens were tested for each WPC formulation. The flexural modulus of elasticity (MOE) and MOR were calculated according to ASTM D790-10 (2010).

Artificial weathering

FR-incorporated WPC specimens at a loading level of 15% (w/w) and a control WPC specimen were placed in a xenon arc-type light-exposure apparatus operated according to ASTM D2565-99 (2008). The specimens were mounted in four rows on a drum that rotated around a xenon arc lamp at 1 rpm. The exposure cycle consisted of 102 min of light and 18 min of simultaneous water spray and light. The specimens were removed for cone calorimetry tests after 2000 h of exposure. Two replicate specimens were tested.

Statistical analyses

To confirm the homogeneity of the test population, all of the data was analyzed by a one-way analysis of variance (ANOVA), and the results were then statistically compared by Tukey’s test (Vargas 1999).

RESULTS AND DISCUSSION

Cone Calorimetry Test Results for the Un-Weathered Specimens

The HRR, broadly defined as the rate at which heat is generated from a fire, is the most important parameter for assessment of the fire hazard of a given material. The HRR is decreased with the addition of FRs (Babrauskas and Peacock 1992; Grexa and Lübke 2001; Mouritz and Gibson 2007).

Different types of materials have typical burning behaviors that have characteristic HRR *vs.* time curves. In this study, type d HRR curves were detected for all of the test specimens. The initial peak HRR values were recorded as PHRR. (Schartel and Hull 2007; Hamdani *et al.* 2009). The peaks and averages derived from the heat release curves of test specimens are reported in Figs. 1 to 4 and Tables 2 and 3.

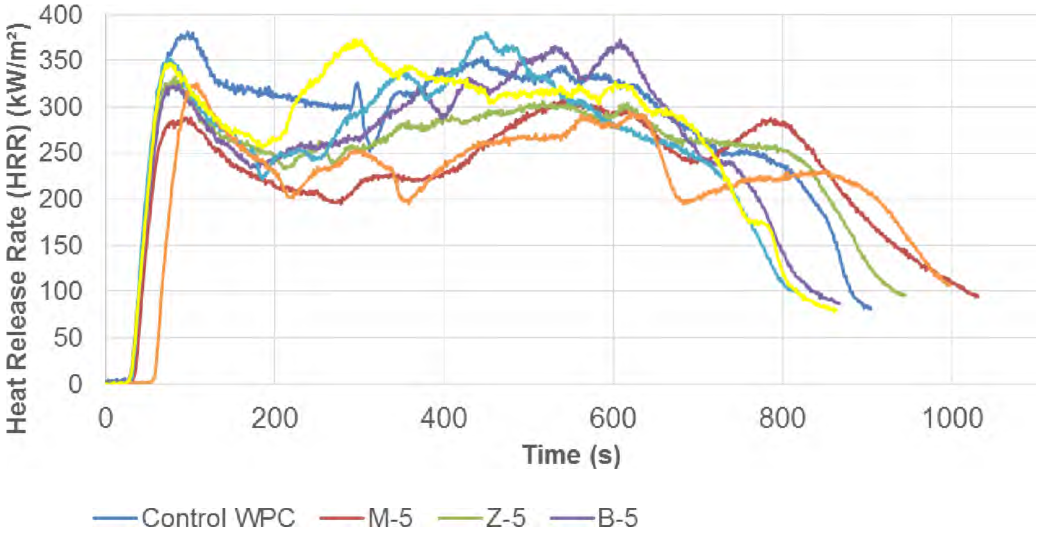

Fig. 1. HRR curves for the control WPC and FR-incorporated WPCs at a loading level of 5% (w/w)

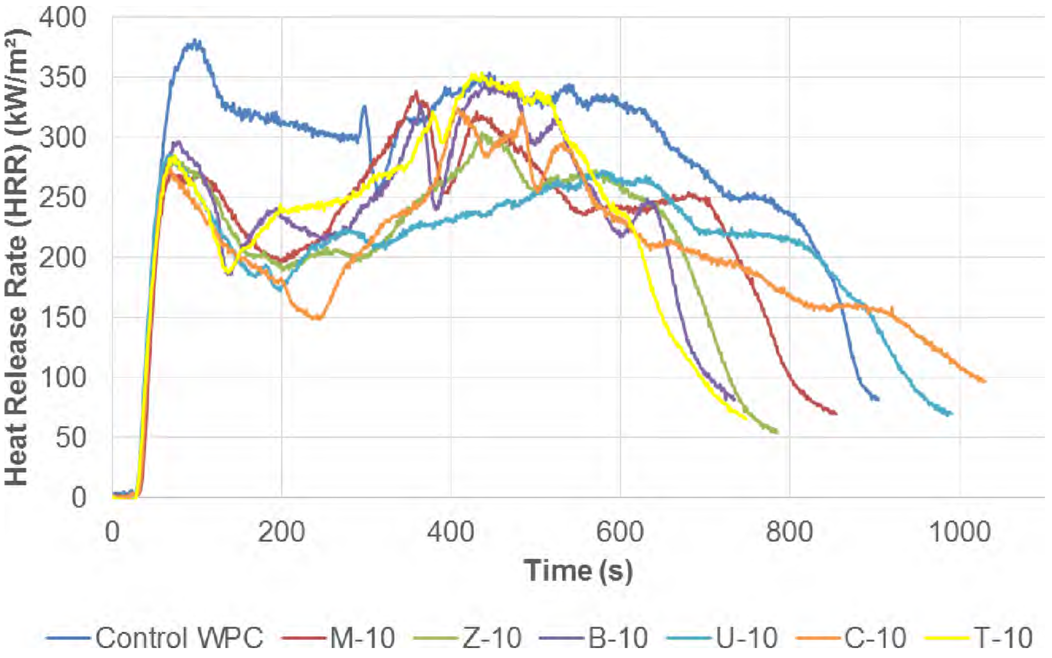

Fig. 2. HRR curves for the control WPC and FR-incorporated WPCs at a loading level of 10% (w/w)

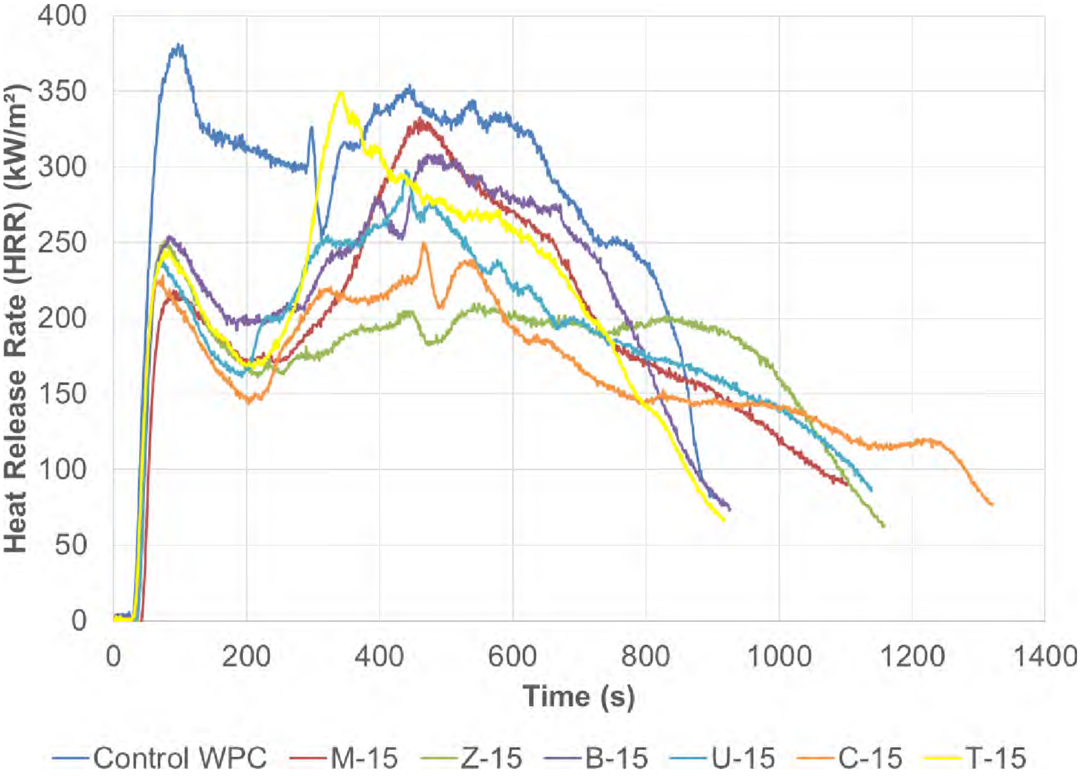

Fig. 3. HRR curves for the control WPC and FR-incorporated WPCs at a loading level of 15% (w/w)

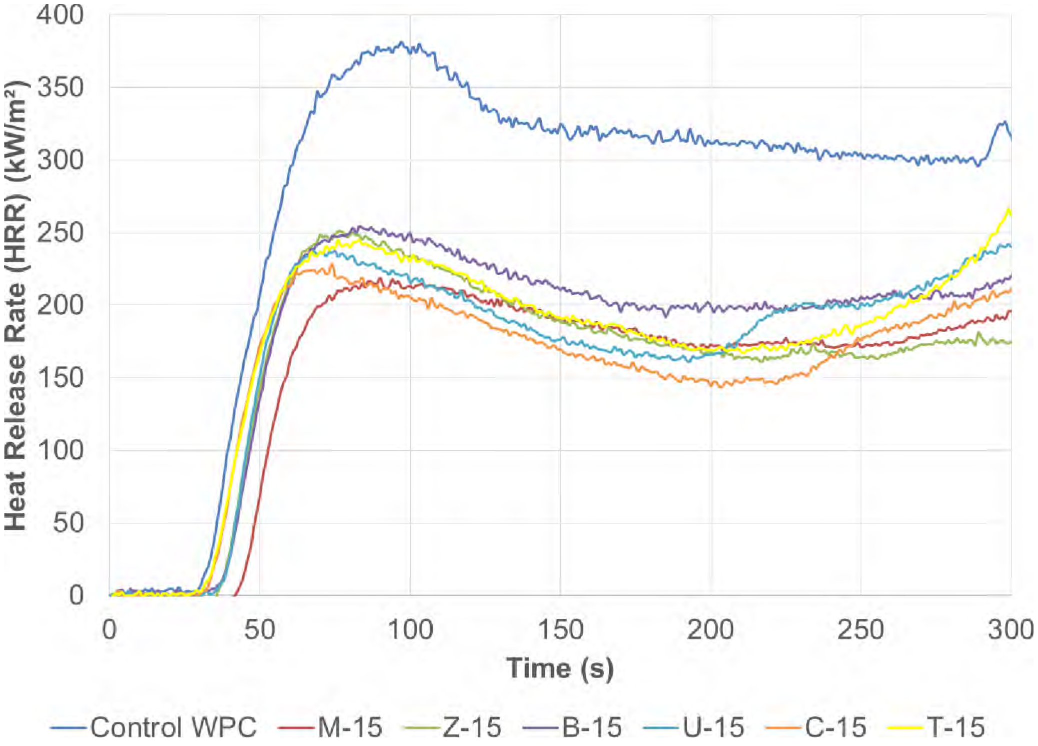

Fig. 4. First 5 min of the HRR curves for the control WPC and FR-incorporated WPCs at a loading level of 15% (w/w)

Table 2. Cone Calorimetry Test Results of the Control WPC and FR-Incorporated WPCs at Loading Levels of 5%, 10%, and 15% (w/w)

Specimens	TTI		PHRR		Time for PHRR		av-HRR (kW/m^2)					
	s	std. dev.	kW/m2	std. dev.	s	std. dev.	60 s	std. dev.	180 s	std. dev.	300 s	std. dev.
Control WPC	28.4	0.9	381.3	1.6	96.0	3.6	246.9	3.3	305.9	1.9	307.9	8.4
M-5	34.2	2.2	292.2	9.5	93.3	8.0	214.1	8.6	235.2	6.4	225.8	5.9
M-10	34.4	1.8	271.2	4.0	91.0	17.6	205.8	8.1	222.2	3.8	227.4	5.8
M-15	42.2	1.6	218.9	1.6	85.7	5.1	170.3	5.6	180.8	0.6	177.9	4.6
Z-5	28.5	0.6	333.0	0.3	81.7	2.5	226.9	3.6	255.5	0.9	253.1	2.5
Z-10	33.1	2.5	284.9	1.4	68.3	2.3	221.4	9.0	220.2	5.2	222.8	16.6
Z-15	35.5	1.3	252.1	5.9	76.3	0.6	192.1	3.2	191.0	2.3	182.5	8.5
B-5	30.1	3.5	325.0	6.6	80.0	0.0	225.3	13.0	253.0	5.7	259.0	5.8
B-10	30.8	0.7	297.4	5.8	76.7	3.5	220.1	3.5	230.0	2.0	241.5	11.4
B-15	36.4	1.0	254.2	6.4	78.0	7.0	201.1	8.8	207.5	3.4	213.2	12.7
C-5	28.1	2.9	327.1	6.7	75.7	3.8	228.2	10.2	241.6	5.5	241.2	9.9
C-10	30.2	1.4	278.5	7.9	67.7	1.2	203.0	7.2	204.1	2.9	201.9	6.8
C-15	32.3	3.7	227.6	8.0	67.3	7.4	179.3	5.0	174.0	4.5	170.9	8.3
U-5	28.6	1.0	352.6	6.1	75.3	1.5	244.1	6.4	261.7	1.9	280.3	16.6
U-10	30.1	1.7	282.5	9.2	67.3	1.5	209.4	4.8	206.6	5.7	215.2	6.8
U-15	36.6	1.1	238.1	2.4	72.0	2.6	188.1	2.0	181.8	3.1	187.6	11.9
T-5	27.6	2.4	345.0	9.6	77.0	1.7	231.9	12.6	266.8	7.8	285.8	10.7
T-10	28.8	1.4	288.7	7.4	71.3	2.3	207.3	7.4	221.7	6.6	232.2	2.8
T-15	32.4	3.0	245.5	3.4	77.0	2.8	182.6	1.4	193.7	1.8	204.8	0.8

TTI – time to ignition; PHRR – peak heat release rate; av-HRR – average heat release rate

The HRR and TTI values relate important information on the first stage of fire development within the first 3 min after ignition (Babrauskas and Peacock 1992; Arao *et al.* 2014). In a recent study, the TTI of the FR-incorporated WPCs were remarkably longer than that for the control WPC specimens, especially at a loading level of 15% (w/w). The highest TTI was recorded for the magnesium hydroxide-incorporated WPC specimens at a loading level of 15% (w/w). The second highest TTI was observed in the ulexite-incorporated WPC specimen at the same loading level.

As was expected, increasing the amount of FR decreased the PHRR (Table 2). This was directly related to a decrease in the amount of HDPE in the WPC. The results showed that the most important reduction in the initial PHRR values was recorded in the magnesium hydroxide- and colemanite-added WPCs at a loading level of 15% (w/w). The amount of reduction in the PHRR values of the WPCs incorporated with magnesium hydroxide and colemanite at a loading level of 15% (w/w) was determined to be 42% and 40%, respectively, when compared with the control WPC specimen. Ulexite and tincalconite reduced the PHRR by approximately 38% and 36%, respectively, at a loading level of 15% (w/w). In contrast, the lowest reduction to the PHRR obtained, which was with the borax- and zinc borate-added WPC specimens, was approximately 33% at the same loading level (Figs. 3 and 4).

Table 3. Calculated THR, FGI, AEHOC, and ASEA for the Control WPC and FR-Incorporated WPCs at Loading Levels of 5%, 10%, and 15% (w/w)

Specimens	THR		FGI	AEHOC		ASEA	
	MJ/m^2	std. dev.	$kW/m^2 \cdot s$	MJ/kg	std. dev.	m2/kg	std. dev.
Control WPC	246.8	10.8	13.4	31.1	0.1	376.5	47.0
M-5	231.0	4.5	8.5	29.6	0.2	277.2	22.5
M-10	188.9	2.4	7.9	25.9	0.1	245.8	30.8
M-15	215.0	3.3	5.2	23.4	0.3	183.0	4.2
Z-5	237.0	4.2	11.7	30.1	0.2	353.0	32.7
Z-10	167.9	3.9	8.6	25.2	0.7	263.5	24.5
Z-15	204.8	10.8	7.1	23.8	0.5	246.3	22.1
B-5	223.6	4.6	10.8	29.9	0.9	275.5	11.5
B-10	168.6	4.0	9.7	26.5	0.2	253.0	31.6
B-15	197.2	5.0	7.0	25.3	0.5	186.0	24.6
C-5	224.7	3.4	11.6	29.1	0.6	329.4	18.3
C-10	207.0	1.6	9.2	25.7	0.4	232.4	22.8
C-15	213.5	0.9	7.0	24.8	0.2	201.9	15.5
U-5	226.6	12.0	12.3	30.7	0.0	341.7	82.3
U-10	205.0	3.7	9.4	25.9	0.2	264.7	49.9
U-15	209.7	4.4	6.5	24.1	0.1	215.7	24.6
T-5	236.0	11.4	12.5	30.5	0.4	266.9	13.2
T-10	174.1	1.8	10.0	25.9	0.3	256.1	29.9
T-15	195.5	3.2	7.6	24.8	0.8	227.0	45.0

THR – total heat release; FGI – fire growth index; AEHOC – average effective heat of combustion; ASEA – average specific extinction area

The average HRRs (av-HRRs) (Table 2; Fig. 4) of the FR-incorporated WPCs were significantly lower than those for the control WPC specimens, especially at a loading level of 15% (w/w). The lowest av-HRR recorded for the colemanite-incorporated WPC specimen with a loading level of 15% (w/w) occurred during the first 180 to 300 s. The second lowest av-HRR in the same time period was recorded in the magnesium hydroxide-incorporated WPC specimens at the same loading level. In contrast, the lowest av-HRR value recorded in the first 60 s was with the magnesium hydroxide-incorporated WPC specimens at a loading level of 15% (w/w).

The fire growth index (FGI) was used to define the flashover potential of specimens as a fire hazard. The FGI was defined as the PHRR/TTI and a higher ratio of PHRR/FGI indicated a higher propensity for flashover (Babrauskas 1984; Petrella 1994; Işitman 2012). The highest FGI was calculated for the control WPC specimens and the lowest FGI value was determined for the magnesium hydroxide-incorporated WPC specimen at a loading level of 15% (w/w). The second lowest FGI was recorded with the ulexite incorporated-WPC specimens at a loading level of 15% (w/w). Colemanite had a better performance than zinc borate at a 15% (w/w) loading level based on the FGI (Table 3).

The average effective heat of combustion (AEHOC) was calculated by dividing the total heat released (THR) with the total mass loss. This value corresponds mostly to the flaming combustion condition (Grexa and Lübke 2001). Lower AEHOC values are a desirable property for FR-treated products and reflect better fire performance characteristics. Based on the AEHOC values, all of the chemicals improved the fire performance of the WPCs when compared with the control WPC specimens. The most important decreases in the AEHOC values were observed at loading levels of 10% and 15% (w/w) when compared with the control WPC specimens (Table 3).

The average specific extinction area (ASEA) value is an indication of the amount of visible smoke generated (Table 3). Higher ASEA values reflect a larger amount of visible smoke being generated from the material during the fire test. The ASEA value (m^2/kg) could be explained as a measure of smoke obscuration averaged over the whole test period. This value also reflects the smoke production rate (Li 2000; Zhao *et al.* 2006; Terzi 2015). Most deaths that occur during a fire are not dependent on the heat or flame. Most people lose direction during evacuation because of thick smoke from the fire. This situation increases the exposure time to toxic gases and raises the probability of death during a fire. Consequently, smoke production is an important fire reaction property of the material (Mouritz and Gibson 2007). Even though all of the chemicals tested showed smoke suppressant properties, magnesium hydroxide and borax at a loading level of 15% (w/w) were the most effective. The ASEA values of these specimens (magnesium hydroxide and borax at 15%) decreased by half compared with the control WPC specimens. Colemanite, ulexite, and tincalconite at a loading level of 15% were more effective than zinc borate at reducing the ASEA values of the control WPC specimens.

Cone Calorimetry Test Results after the Artificial Weathering Process

The peaks and averages derived from the curves of the artificial weathered and un-weathered specimens are reported in Tables 4 and 5. After the weathering process, the TTIs of the specimens were shorter than those of the un-weathered group, except for the magnesium hydroxide-incorporated WPC specimens. The TTI ranking was as follows: Control WPC < C < T < Z < B < U < M. It then changed after the artificial weathering process to: Control WPC < C < T < B < U < Z < M. The magnesium hydroxide-incorporated WPC specimens had the longest TTI in both situations. The boric acid-added WPC specimens were affected significantly by the weathering process and the TTI became shorter than that of the un-weathered specimens by 12%. In contrast, the TTI for the weathered magnesium hydroxide-added WPC specimens was determined to be 13.5% longer than for the un-weathered magnesium hydroxide-added WPCs. Statistically significant differences were found just for the boric acid- and ulexite-incorporated WPC specimens based on the TTI results after the artificial weathering period (Table 4).

The PHRR values of all of the composite specimens increased after the artificial weathering process. The PHRR value ranking was: Control WPC > B > Z > T > U > C > M. After artificial weathering, the ranking changed to: Control WPC > T > B > Z > U > C > M. The tincalconite-incorporated WPC specimen was affected at the maximum ratio, and the PHRR increased by *ca.* 18%. Among the artificially weathered and FR-incorporated WPC specimens, the magnesium hydroxide-incorporated WPC had the lowest PHRR value. Although PHRR was increased by approximately 16% after the artificial weathering process, the second lowest PHRR value was with the colemanite-incorporated WPC specimens. The lowest PHRR increase (5%) was for the control WPC specimen after the artificial weathering process. Statistically significant differences were found for all of the FR-incorporated WPC specimens, except for the boric acid-incorporated WPC specimens (Table 4).

Table 4. Cone Calorimetry Test Results of the Un-Weathered and Artificially Weathered Control WPC and FR-Incorporated WPCs at a Loading Level of 15% (w/w)

Specimens	TTI			PHRR			Time for PHRR			av-HRR (kW/m^2)								
	s	std. dev.		kW/m^2	std. dev.		s	std. dev.		60 s	std. dev.		180 s	std. dev.		300 s	std. dev.	
Control WPC	28.4	0.9	ns	381.3	1.6	ns	96.0	3.6	ns	246.9	3.3	*	305.9	1.9	ns	307.9	8.4	ns
AW-Control WPC	27.7	1.3		401.4	17.2		95.0	1.4		260.9	4.0		317.2	13.6		310.6	18.6	
M-15	42.2	1.6	ns	218.9	1.6	*	85.7	5.1	ns	170.3	5.6	*	180.8	0.6	**	177.9	4.6	ns
AW-M-15	47.9	3.3		245.0	7.3		86.0	1.4		191.8	4.9		195.4	7.1		184.8	6.8	
Z-15	35.5	1.3	ns	252.1	5.9	**	76.3	0.6	**	192.1	3.2	ns	191.0	2.3	ns	182.5	8.5	ns
AW-Z-15	33.2	2.4		286.4	20.2		80.0	1.4		198.2	6.6		203.7	9.0		191.9	5.2	
B-15	36.4	1.0	*	254.2	6.4	ns	78.0	7.0	ns	201.1	8.8	ns	207.5	3.4	ns	213.2	12.7	ns
AW-B-15	32.1	1.2		295.7	25.2		79.5	2.1		192.7	9.3		201.1	17.4		199.3	21.9	
C-15	32.3	3.7	ns	227.6	8.0	*	67.3	7.4	ns	179.3	5.0	*	174.0	4.5	ns	170.9	8.3	ns
AW-C-15	30.3	2.1		271.8	10.5		69.5	0.7		193.5	0.9		183.0	4.9		167.9	13.0	
U-15	36.6	1.1	**	238.1	2.4	*	72.0	2.6	ns	188.1	2.0	*	181.8	3.1	ns	187.6	11.9	ns
AW-U-15	33.1	1.7		283.4	6.5		75.0	0.0		201.2	4.2		190.8	6.0		176.6	4.9	
T-15	32.4	3.0	ns	245.5	3.4	*	77.0	2.8	ns	182.6	1.4	*	193.7	1.8	*	204.8	0.8	ns
AW-T-15	30.8	0.3		300.1	6.5		76.0	0.0		199.7	2.9		209.1	1.0		204.4	8.1	

AW: artificially weathered; *: $p < 0.01$; **: $p < 0.05$; ns: non-significant; Statistical analyses were made between un-weathered and artificially weathered specimens for each boron mineral.

After weathering, there was no difference in the zinc borate-incorporated WPCs based on the THR value. The lowest THR value was recorded for the zinc borate-added WPC specimens. The tincalconite-incorporated WPC specimen was affected at the maximum ratio and the THR value increased by approximately 20%. The THR value ranking was: Control WPC > M > C > U > Z > B > T. After the artificial weathering process (Table 5), the ranking changed to: Control WPC > T > C > M > U > B > Z.

The FGI values of the composite specimens increased after the artificial weathering process, except for the magnesium hydroxide-incorporated WPC specimen. The FGI value ranking was: Control WPC > T > Z > C = B > U > M. After the artificial weathering process, it changed to: Control WPC > T > B > C > Z = U > M. The borax-incorporated WPC specimens were affected at the maximum ratio by the artificial weathering process and the FGI value increased by approximately 32%. Additionally, the FGI values of the ulexite-, tincalconite-, colemanite-, and zinc borate-incorporated WPC specimens increased by approximately 31.5%, 28.5%, 27.5%, and 21.5%, respectively. The FGI value decreased only for the magnesium hydroxide-incorporated WPC specimen and it decreased by 1.5% (Table 5).

Table 5. Calculated THR, FGI, AEHOC and ASEA for the Un-Weathered and Artificially Weathered Control WPC and FR-Incorporated WPCs at a Loading Level of 15% (w/w)

Specimens	THR			FGI	AEHOC			ASEA		
	MJ/m^2	std. dev.		kW/m^2·s	MJ/kg	std. dev.		m^2/kg	std. dev.	
Control WPC	246.8	10.8	**	13.4	31.1	0.1	ns	376.5	47.0	ns
AW-Control WPC	276.2	13.2		14.5	30.6	1.1		378.5	21.3	
M-15	215.0	3.3	ns	5.2	23.4	0.3	*	183.0	4.2	ns
AW-M-15	219.9	2.6		5.1	25.5	0.1		232.3	43.4	
Z-15	204.8	10.8	ns	7.1	23.8	0.5	*	246.3	22.1	ns
AW-Z-15	204.8	5.4		8.6	26.2	0.6		249.8	94.3	
B-15	197.2	5.0	ns	7.0	25.3	0.5	**	186.0	24.6	ns
AW-B-15	212.0	18.9		9.2	26.6	0.5		221.9	90.1	
C-15	213.5	0.9	ns	7.0	24.8	0.2	**	201.9	15.5	**
AW-C-15	224.8	18.0		9.0	26.3	0.7		288.6	31.0	
U-15	209.7	4.4	ns	6.5	24.1	0.1	*	215.7	24.6	ns
AW-U-15	218.0	4.7		8.6	25.6	0.5		194.2	8.5	
T-15	195.5	3.2	*	7.6	24.8	0.8	**	227.0	45.0	ns
AW-T-15	235.8	13.4		9.7	27.3	0.7		220.9	3.8	

AW: artificially weathered; *: $p < 0.01$; **: $p < 0.05$; ns: non-significant; Statistical analyses were made between un-weathered and artificially weathered specimens for each boron mineral.

The AEHOC values of all of the FR-incorporated composite specimens increased after the artificial weathering process. The zinc borate- and tincalconite-incorporated WPC specimens were affected at the maximum ratio by the artificial weathering process and the AEHOC values increased by approximately 10%.

The AEHOC value ranking was previously: Control WPC > B > C = T > U > Z > M. The ranking changed after the artificial weathering process to: Control WPC > T > B > C > Z > U > M. The borax- and colemanite-incorporated WPC specimens were affected at the minimum ratio by the artificial weathering process and the AEHOC values increased by approximately 5.1% and 5.8%, respectively. There were statistically significant differences between the AEHOC values of the weathered and un-weathered WPC specimens, except for the control WPC specimens (Table 5).

The ASEA values of the ulexite- and tincalconite-incorporated WPC specimens decreased by approximately 10% and 2.5%, respectively, after the artificial weathering process. In contrast, the weathering process dominated the smoke production of the colemanite-, magnesium hydroxide-, and borax-incorporated WPC specimens and the ASEA values increased by 43%, 27%, and 19%, respectively. There was a statistically significant difference between the AEHOC values of the weathered and un-weathered colemanite-incorporated WPC specimens (Table 5).

LOI Test Results

The LOI values were used to rank the relative flammability of the test specimens (Mouritz and Gibson 2007). Higher LOI values reflect better fire performance characteristics. Polymeric materials with LOI values greater than 21 can be classified as "self-extinguishing", while polymeric materials with LOI values less than 21 can be classified as "flammable" (Işitman 2012).

In this study, extinguishment was observed below a 21% oxygen level for the ulexite-, colemanite-, tincalconite-, and zinc borate-incorporated WPC specimens at a loading level of 5%. In contrast, extinguishment was observed above an oxygen level of 21% when the loading level increased to 10% and 15% (w/w) for all FR chemicals (Fig. 5).

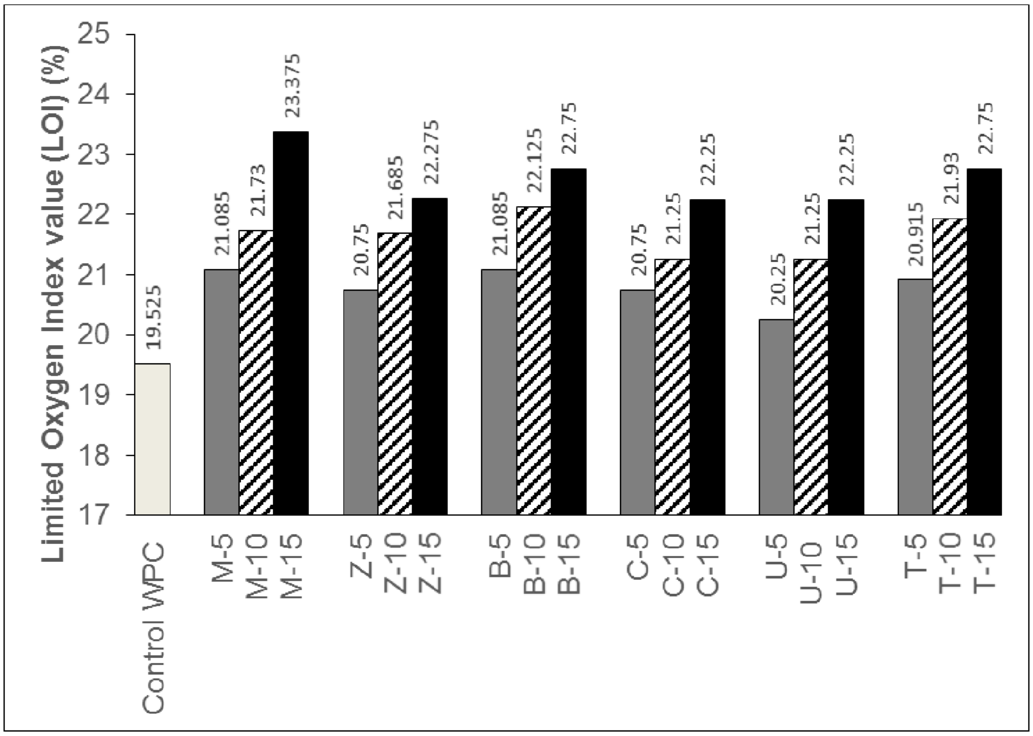

Fig. 5. LOI test results for the control WPC and FR-incorporated WPCs at loading levels of 5%, 10%, and 15% (w/w)

Table 6. Statistical Evaluation of the 3-Point Bending Test Results

MOE Q Values from Pairwise Means

	Specimen	Control WPC	M-15	Z-15	B-15	C-15	U-15	T-15
	Control WPC		-6.756789133	-10.52128594	-8.397723637	-5.695007984	-7.722044723	-6.418949676
	M-15	p < 0.01		-3.764496803	-1.640934504	1.061781149	-0.96525559	0.337839457
	Z-15	p < 0.01	ns		2.123562299	4.826277952	2.799241212	4.102336259
p values	B-15	p < 0.01	ns	ns		2.702715653	0.675678913	1.97877396
2 tailed	C-15	p < 0.01	ns	p < 0.05	ns		-2.02703674	-0.723941693
	U-15	p < 0.01	ns	ns	ns	ns		1.303095047
	T-15	p < 0.01	ns	ns	ns	ns	ns	

MOR Q Values from Pairwise Means

	Specimen	Control WPC	M-15	Z-15	B-15	C-15	U-15	T-15
	Control WPC		-0.534479421	-4.567934586	-4.599008971	0.198876064	-0.950876179	-0.553124052
	M-15	ns		-4.033455165	-4.06452955	0.733355485	-0.416396758	-0.018644631
	Z-15	p < 0.05	ns		-0.031074385	4.766810649	3.617058407	4.014810534
p values	B-15	p < 0.05	ns	ns		4.797885034	3.648132792	4.045884919
2 tailed	C-15	ns	ns	p < 0.05	p < 0.05		-1.149752243	-0.752000115
	U-15	ns	ns	ns	ns	ns		0.397752127
	T-15	ns	ns	ns	ns	ns	ns	

Table 7. 3-Point Bending Test Results for the Control WPC and FR-Incorporated WPCs at a Loading Level of 15% (w/w)

Specimens	MOE[a] (GPa)	SD	MOR[b] (MPa)	SD
Control WPC	2.39	0.55	34.08	5.44
M-15	3.79	0.74	34.94	4.56
Z-15	4.57	0.41	41.43	3.51
B-15	4.13	0.4	41.48	2.47
C-15	3.57	0.27	33.76	1.6
U-15	3.99	0.47	35.61	3.57
T-15	3.72	0.15	34.97	2.55

[a] modulus of elasticity; [b] modulus of rupture

The LOI values increased by nearly 21% in the magnesium hydroxide-incorporated WPCs at a loading level of 15% (w/w) when compared with the control WPC specimens. The second highest increase (nearly 16%) in the LOI values occurred when borax and tincalconite were incorporated at a loading level of 15% (w/w). Incorporation of colemanite and ulexite into WPCs increased the LOI levels by nearly 13% at the same loading level.

3-Point Bending Test

The effect of the FRs on the mechanical properties is shown in Tables 6 and 7. It was observed that all of the FRs statistically affected the measured MOE values. In particular, the incorporation of zinc borate and borax increased the MOE by approximately 48% and 42%, respectively. Zinc borate significantly increased the MOE value when compared with the colemanite. The lowest improvement to the MOE values (approximately 33%) was recorded for the colemanite-incorporated WPCs. Ulexite provided the highest improvement to the MOE values (40%) among the boron minerals used. Similar to the effect on the MOE values, zinc borate and borax had the greatest improvement on the MOR (approximately 18%). The other FRs did not statistically affect the MOR values when compared with the control WPC specimens.

CONCLUSIONS

1. Based on the cone calorimetry test, LOI, and 3-point bending test results, it was determined that boron minerals could be used as FRs in place of commercial zinc borate and magnesium hydroxide to enhance the fire performance of WPCs.
2. In particular, colemanite showed the best cone calorimetry test performance according to the PHRR values without any flexural properties loss when compared with the other boron minerals. This performance was attributed to the higher boron content and its thermal properties. When colemanite was exposed to heat, it showed the same thermal behaviors as magnesium hydroxide-incorporated WPCs (See SUPF1). As can be seen from the thermogravimetric curves, colemanite started to degrade near 270 °C and finished degrading at 425 °C, while magnesium hydroxide degraded from 273 to 418 °C. The heat flow profiles of magnesium hydroxide and colemanite may have indicated that these additives have a heat sink effect *via* endothermic reactions over similar

temperature ranges.

3. Colemanite can be considered to be a reasonable FR if used at a loading level of at least 15% (w/w) in WPCs based on its low-cost properties and considerably low environmental concerns. Colemanite does not contain any heavy metals in its chemical formulation, such as zinc, copper, mercury, lead, cadmium, *etc.*, and commercial zinc borate and magnesium hydroxide are approximately five and two times more expensive than colemanite, respectively.
4. It was determined that colemanite could be combined with a smoke suppressant additive for a better FR performance. These properties could make the colemanite a good alternate additive for different kinds of composites, such as natural fiber-based composites, hybrid polymer composites, *etc.* As was expected, the lowest increase in the PHRR value after the artificial weathering process was found with the control WPC specimen because of the highest HDPE percentage.

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