Effects of Boron Compounds on the Mechanical and Fire Properties of Wood-chitosan and High-density Polyethylene Composites

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Wood-plastic composites (WPCs) represent a growing class of durable, low-maintenance construction materials whose use can decrease dependence on petroleum. High-density polyethylene (HDPE), chitosan (CS), wood flour (WF), boric acid (BA), and borax (BX), as well as maleic anhydride grafted polyethylene (MAPE) and polyethylene wax (PE wax), were used to develop a durable wood-plastic composite (WPC) using the extrusion method. The effects of boron compounds (3%, 6%, 9%, or 12% by weight BA/BX) on the mechanical and fire properties of the WPCs were investigated. Mechanical testing indicated that as the percentage weight of boron compounds increased, the flexural modulus, flexural strength, and tensile strength significantly decreased. Cone calorimeter tests were used to characterize the fire performance of the WPCs, and these results suggested that adding BA/BX compounds to WPCs modestly improved the fire performance. As the percentage weight of BA/BX increased from 3% to 9%, the time to ignition (TTI), heat release rate (HRR), total heat release rate (HRR-Total), smoke production rate (SPR), and specific extinction area (SEA) of the WPCs were all reduced.

Keywords: Wood flour; Chitosan; High-density polyethylene; Mechanical; Fire retardant; Boron compounds

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INTRODUCTION

Wood-plastic composites (WPCs) represent an emerging class of materials that combine the favorable performance and cost attributes of both wood and plastics and act as an environmentally friendly way to increase the use of recycled plastics (Faruk *et al.* 2007; Clemons 2002). However, WPCs present potential fire hazards; thus, it is necessary to improve our understanding of both the fire performance and the effects of fire retardants (FRs) on these products. Because WPCs have the potential to be widely used in products such as decking, furniture, electrical casings, industrial flooring, interior decorations, insulation, automobile parts, and architectural materials, developing safe and durable WPCs is critical.

Since the late 1970s, boron compounds such as borax (BX), boric acid (BA), and zinc borate (ZB) have been used as FRs in the plastics industry. Boron compounds have also been used as fungicides and insecticides for wood preservation and are especially effective against termites (Ayrilmis 2013). Boron-based buffers have also been used as additives in FR treatments and have been found to significantly reduce the severity of thermal degradation (Wu *et al.* 2010; Nagieb *et al.* 2011). A mixture of BA and BX has been found to effectively retard flame spread and smoldering (Chai *et al.* 2012). Although boron compounds reduce the spread of flame in wood, they may have diverse effects on the mechanical properties and hygroscopicity of WPCs (Nagieb 2011); therefore, more research in this area is warranted.

Chitin is the second most abundant natural polysaccharide after cellulose, and it possesses excellent mechanical and thermal properties (Martinez *et al.* 2010; Ou *et al*. 2010). Chitosan (CS), a derivative of chitin, is a linear polysaccharide that originates from the shells of crustaceans such as crab and shrimp. It is a widely available, low-cost product with high biocompatibility and anti-microbial properties (Khor and Lim 2003). Chitosan also has a low fiber/matrix adhesion ratio (Mir *et al*. 2011) and a large number of commercial uses. Therefore, CS was chosen as a WPC component for this study.

The fire performance of WPCs is not well understood, and there is little information regarding the effectiveness of various FRs on WPCs (Ayrilmis *et al*. 2012). This study used high-density polyethylene (HDPE), CS, wood flour (WF), BA/BX, maleic anhydride grafted polyethylene (MAPE), and PE wax as a lubricant to develop a durable and flame-resistant WPC with the extrusion method. The primary objective of this study was to investigate the effects of boron compounds on the mechanical and FR properties of WPCs.

EXPERIMENTAL

Materials

Poplar (*Populus tremula*) wood flour was obtained from the Xingrong Wood-fiber Company in Harbin, China. Particle size ranged from 20-mesh to 40-mesh. The wood-flour was dried in a laboratory oven at 103 °C ± 2 °C for 12 h to a moisture content of 3% to 4% (based on the oven-dry weight of the wood), and was then stored in a polyethylene bag. Eighty-five percent de-acetylated CS was obtained from the HuaiFang Chemical Company in Shandong, China. The high-density polyethylene (HDPE) resin (5000 S) used in this work was purchased from DaQing Petrifaction Co., Ltd. in DaQing, China. Boric acid (BA) (H_3BO_3) (q = 1.7 g/cm^3, crystalline solid form) and borax (BX) ($Na_2B_4O_7.10H_2O$) (q = 1.4 g/cm^3, crystalline solid form) (BA/BX, 1:1 by weight) were manufactured by the Shanghai Chemical Company of China. Maleic anhydride grafted polyethylene (MAPE) was manufactured by Fengyuan Co., Ltd. in Guangzhou, China. All additives were industrial products.

Methods

Sample preparation

Samples of WPCs were prepared according to the compound formulations shown in Table 1. All of the components were mixed in a high-speed blender (SHR-10A, Zhangjiagan, China) with a rotation speed of 80 revolutions per minute (rpm) for 5 min. Composites were then extruded by a twin-screw extruder (SJSH30/SJ45, Nanjing, China) with a rotation speed of 50 rpm. Temperature was controlled and ranged from 155 to 165 °C. The samples were then extruded by a sign-screw extruder with a rotation speed of 10 rpm. Again, temperature was controlled and ranged from 150 to 160 °C. Finally, mechanical test samples were cut for tensile strength (with dimensions of 160 mm × 13 mm × 4 mm) and flexural strength and flexural modulus (80 mm × 13 mm × 4 mm).

Cone calorimeter test samples were cut with dimensions of 100 mm × 100 mm × 4 mm. Decay resistance test samples were cut with dimensions of 80 mm × 100mm × 4 mm.

Table 1. Mixing Ratios of Raw Materials in Weight Percentage and their Codes

Code	WF	CS	HDPE	MAPE	PE Wax	BA/BX
A	56.4	3.6	36.0	4.0	2.0[a]	0.0
B_1	56.4	3.6	36.0	4.0	2.0[a]	3.0[b]
B_2	56.4	3.6	36.0	4.0	2.0[a]	6.0[b]
B_3	56.4	3.6	36.0	4.0	2.0[a]	9.0[b]
B_4	56.4	3.6	36.0	4.0	2.0[a]	12.0[b]
A_1	60.0	0.0	36.0	4.0	2.0[a]	0.0
B_5	60.0	0.0	36.0	4.0	2.0[a]	3.0[b]
B_6	60.0	0.0	36.0	4.0	2.0[a]	6.0[b]
B_7	60.0	0.0	36.0	4.0	2.0[a]	9.0[b]
B_8	60.0	0.0	36.0	4.0	2.0[a]	12.0[b]
BA/BX = 1:1 by weight						

A = control sample. [a] = PE wax loading content is a total of (WF+CS+HDPE+MAPE)*2%. [b] = BA/BX loading content is a total of (WF+CS+HDPE+MAPE)* % BA/BX (of 3%, 6%, 9%, or 12%). and total (WF%+CS%+HDPE%+MAPE%) = 100%.

Mechanical testing

Tensile strength and flexural strength and modulus were tested following the ASTM standard D790, using an Instron, model RGT-20A (Norwood, MA, USA) device. Tests were carried out at 20 °C and 40% relative humidity. Crosshead speeds were 5 mm/min for tensile tests and 2 mm/min for flexural tests using type-6 samples. Test conditions were selected from the values recommended by the International Organization for Standardization (ISO). Statistical analyses using one-way analysis of variance (ANOVA) were conducted using SPSS v10.0 (SPSS, Chicago, IL, USA).

Cone calorimeter testing

A Fire Testing Technology Limited (FTT) cone calorimeter (manufactured in the UK) was used for fire testing. According to ISO 5660-1 standards, data were taken from the FTT cone calorimeter at a heat flux of 50 kW/m^2. Samples were placed on a horizontal sample holder and were protected from bending or expanding during the heating process by a stainless steel grid. In the cone calorimeter tests, the initial peak heat release rate (Peak HRR, kW/m^2), heat release rate at 60 s and 300 s (HRR-60s and HRR-300 s, MJ/m^2), total heat release rate (HRR-Total, MJ/m^2), effective heat of combustion (EHC, MJ/m^2), mass loss rate (MLR, g/s), specific extinction area (SEA, m^2/kg), total smoke production rate (SPR kW/m^2), and total oxygen consumed (g) were all measured as a function of time. The observation of time to ignition (TTI, s) was also recorded.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) measurements were performed on a Perkin-Elmer Pyris6 Thermal Analyzer under nitrogen flow, from 20 °C to 700 °C at a heating rate of 10 °C /min. The degradation temperature was expressed as the onset temperature of mass loss.

Decay test

Fungal decay tests were carried out according to the classification criteria proposed by Silva *et al.* (2007) except that the specimens were replaced by the 80 mm × 10 mm × 4 mm thick specimens, using a brown-rot fungus and a white rot fungus. Then, they were incubated at 26 ^{o}C for 12 weeks. Test results were expressed as percentage of weight losses of WPCs specimens due to fungal attacks after decay test. Three replicates were used for each decay fungus. The weight loss was calculated and expressed in percent as follows,

$$\text{Weight loss\%} = \frac{W_0 - W_1}{W_0} \times 100 \tag{1}$$

where the initial weight (W_0) is the weight of the specimens prior to fungal exposure and the final weight (W_1) is the weight of specimens after fungal exposure.

RESULTS AND DISCUSSION

Mechanical Properties

One-way analysis of variance (ANOVA) tests indicated that the tensile strength ($P < 0.002$), flexural strength ($P < 0.0001$), and flexural modulus ($P < 0.0001$) with the CS WPCs significantly decreased with the addition of BA/BX, while the flexural strength and flexural modulus without CS WPCs were not significantly affected except for the tensile strength (Tables 2A and 2B).

Table 2. Means with Standard Error and Results of ANOVA for Tensile Strength, Flexural Strength, and Flexural Modulus of WPCs with Different Weight Percentages of BA/BX

Table 2A. ANOVA

With CS		Sum of Squares	df	Mean Square	F	Sig.
Tensile Strength	Between Groups	88.962	4	22.240	6.048	0.002
	Within Groups	91.936	25	3.677		
	Total	180.898	29			
Flexural Strength	Between Groups	4.171	4	1.043	8.030	0.0001
	Within Groups	309.929	25	12.397		
	Total	907.451	29			
Flexural Modulus	Between Groups	4.171	4	1.043	8.030	0.0001
	Within Groups	3.246	25	0.130		
	Total	7.418	29			
Without CS		Sum of Squares	df	Mean Square	F	Sig.
Tensile Strength	Between Groups	66.146	4	16.536	8.666	0.0001
	Within Groups	47.708	25	1.908		
	Total	113.853	29			
Flexural Strength	Between Groups	138.799	4	34.700	2.055	0.117
	Within Groups	422.229	25	16.889		
	Total	561.028	29			
Flexural Modulus	Between Groups	3.294	4	0.824	2.016	0.123
	Within Groups	10.213	25	0.409		
	Total	13.507	29			
*The mean difference is significant at the 0.05 level.						

Table 2B. Means and Standard Error of Mechanical Properties

Composite Code	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)
A	44.55 (1.17)a	70.83 (4.69)a	4.48 (0.57)a
B_1	44.07 (2.02)a	69.76 (3.70)a	4.09 (0.30)a
B_2	41.42 (2.82)b	65.09 (2.91)c	4.08 (0.34)ab
B_3	41.03 (1.80)b	60.46 (4.18)b	3.59 (0.33)bc
B_4	40.25 (1.33)b	60.23 (0.55)b	3.42 (0.11)c
A_1	39.21(1.04)a	67.16(2.96)a	4.33(0.37)a
B_5	40.57(0.99)a	70.93(3.28)a	4.04(0.58)b
B_6	40.74(1.16)a	66.61(2.31)b	3.46(0.90)b
B_7	38.39(1.95)b	65.07(2.64)b	3.90(0.15)b
B_8	37.30(1.53)c	65.05(7.26)b	3.49(0.86)b
Means with different letters for each property are significantly different at the 0.05 level of Within Groups.			

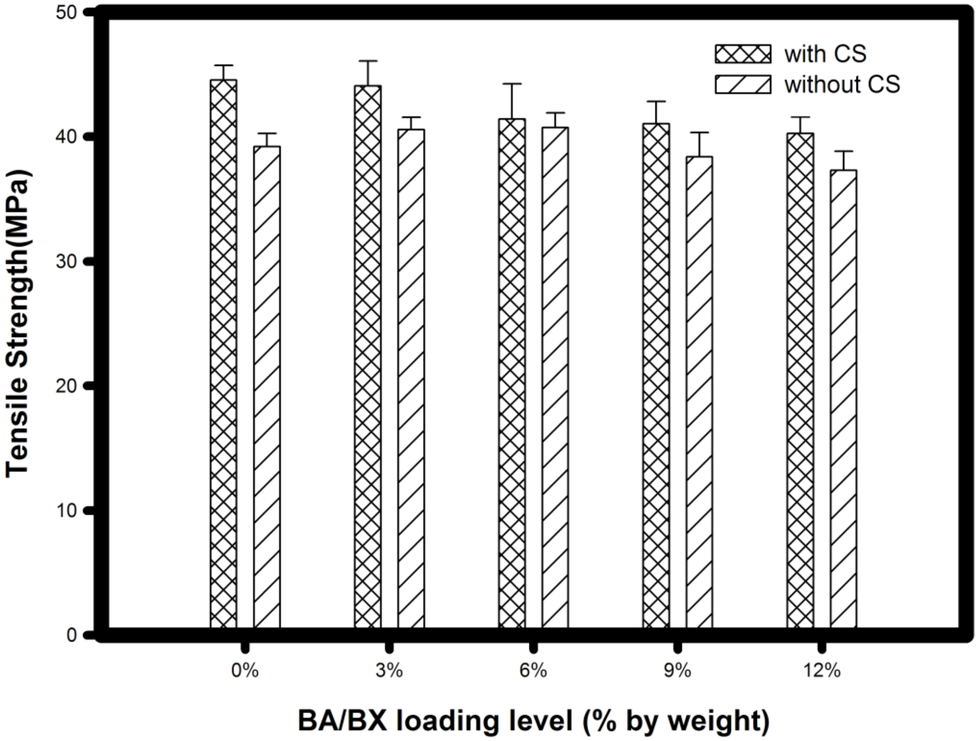

Fig. 1. Tensile strength of WPCs with different BA/BX loadings

Tensile strength

Figure 1 demonstrates that the tensile strength of WPC samples with CS was significantly decreased with increasing BA/BX content. Compared with the control, the tensile strengths of the 9% and 12% BA/BX WPC samples decreased by 7.9% and 9.7%, respectively. Some studies have reported deterioration of the mechanical properties of filled and unfilled plastics with the addition of FRs, as well as a decrease in the tensile strength of filled plastics (Sain *et al.* 2004; Chiu and Wang 1998; Horn 2000). The present study indicated that this may be attributed to poor compatibility between the wood flour and polymer matrix due to the increased surface contamination of the wood flour by the presence of loosely adhering crystalline deposits of the boron compounds. Another reason was that the boron compounds could interfere with the compatibilizer (Ayrilmis 2013; Kurt and Mengeloglu 2011; Wang *et al.* 2007; Ayrilmis *et al.* 2012). However, Fig. 1 demonstrates that the tensile strength of samples without CS WPC first increased and then decreased with increasing BA/BX content. This finding was consistent with previous studies (Ayrilmis *et al.* 2012). The cited study reported that tensile strength of the wood–polypropylene composites samples first increased and then decreased with increasing BA/BX content (from 4% to 12%).

The importance of coupling agent to WPCs has been demonstrated in many studies (Lu *et al* 2000; Wielage *et al.* 2003; Leu *et al.* 2012; Lu *et al*. 2005; Balsuriya *et al*. 2002; Matuana *et al*. 2001; Kazayawoko *et al*. 1997). Over 40 coupling agents have been used in WPCs (Lu *et al* 2000). Leu *et al.* (2012) indicated that coupling agents are organic, inorganic, or hybrid compounds that can improve the compatibility and adhesion between the hydrophilic wood fiber and the hydrophobic polymers. Wielage *et al.* (2003) showed that using a low-molecular weight coupling agent can dramatically increase the tensile strength of WPCs by better wetting the wood fibers, but addition of the coupling agent also caused a slight decrease of the flexural strength. Ayrilmis (2013) evaluated the tensile strength of WPC samples with BA/BX and MAPE content (from 4% to 12% and from 2% to 6%), respectively. It was estimated that boron compounds stopped most of the esterification reactions between hydroxyl on the wood-fiber surface and anhydride on the polyethylene chain, which were replaced by the reactions between the boron and MAPE. In addition, the decrease in the polymer content of the WPC, as a function of the increase in the boron content, caused a reduction in the tensile strength. When the boron content in the WPC increases, the amount of the plastic as the adhesive decreases. Lu *et al.* (2005), Balsuriya *et al.* (2002), Matuana *et al.* (2001), and Kazayawoko *et al.* (1997) observed increases in the tensile strength and stiffness, which is attributed to the improved interfacial bonding between the wood flour and the HDPE matrix as well as the modification of individual components. That was due to the formation of ester bonds between the anhydride carbonyl groups of MAPP and hydroxyl groups of the wood fibers, showing that anhydride moieties of functionalized polyolefin coupling agents entered into an esterification reaction with the surface hydroxyl groups of wood flour. Upon esterification, the exposed polyolefin chains diffuse into the HDPE matrix phase and entangle with HDPE chains during hot pressing.

Flexural strength and modulus

Figure 2 demonstrates that the flexural strength of treated samples decreased moderately with increasing BA/BX content (from 3% to 12%). The maximum percentage of reduction in flexural strength (9.65%) occurred in the 12% BA/BX sample with CS. There were no significant differences in samples without CS. Adhikary *et al*. (2008) observed that the flexural strength exhibits a similar trend to the tensile strength although less variation is observed in the flexural strength with different formulations than the tensile strength. And the flexural MOE of the composites increases with the wood content. With a similar trend to the tensile test results, the addition of the coupling agents significantly improves the flexural strength as well as the stiffness of the composites. Due to the similar mechanism as explained in the previous section, the flexural strength of composites depended on MAPP coupling agent. A similar trend was observed for flexural modulus values as is seen in Fig. 3. Compared with the control sample, the maximum

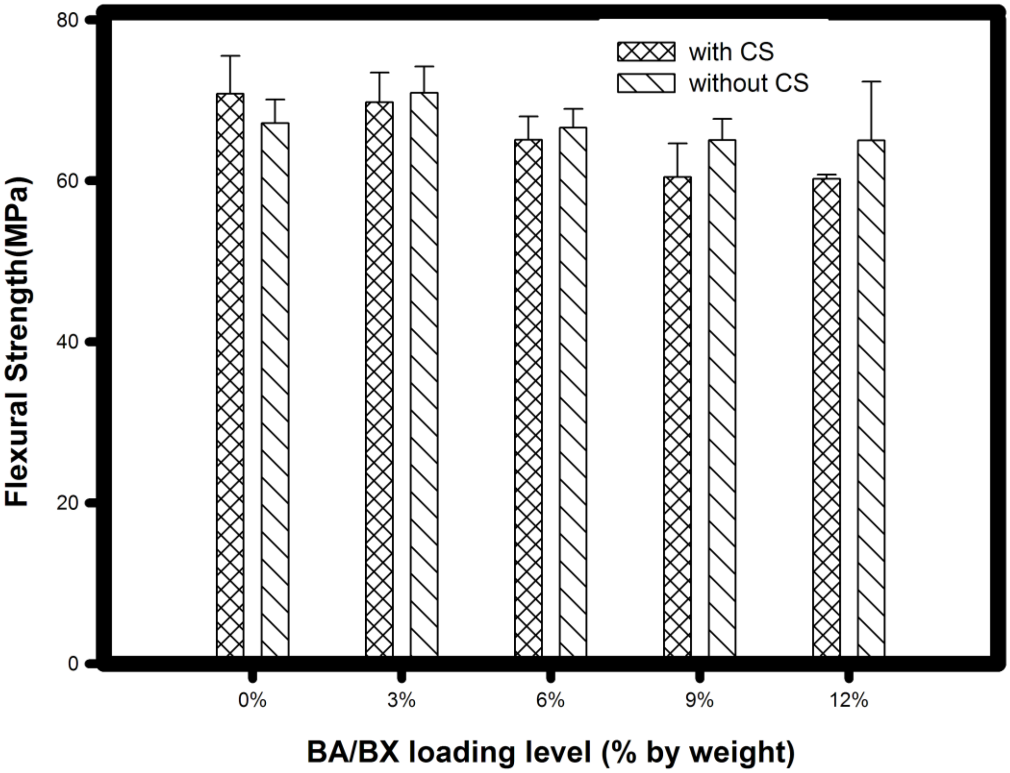

Fig. 2. Flexural strength of WPCs with different BA/BX loadings

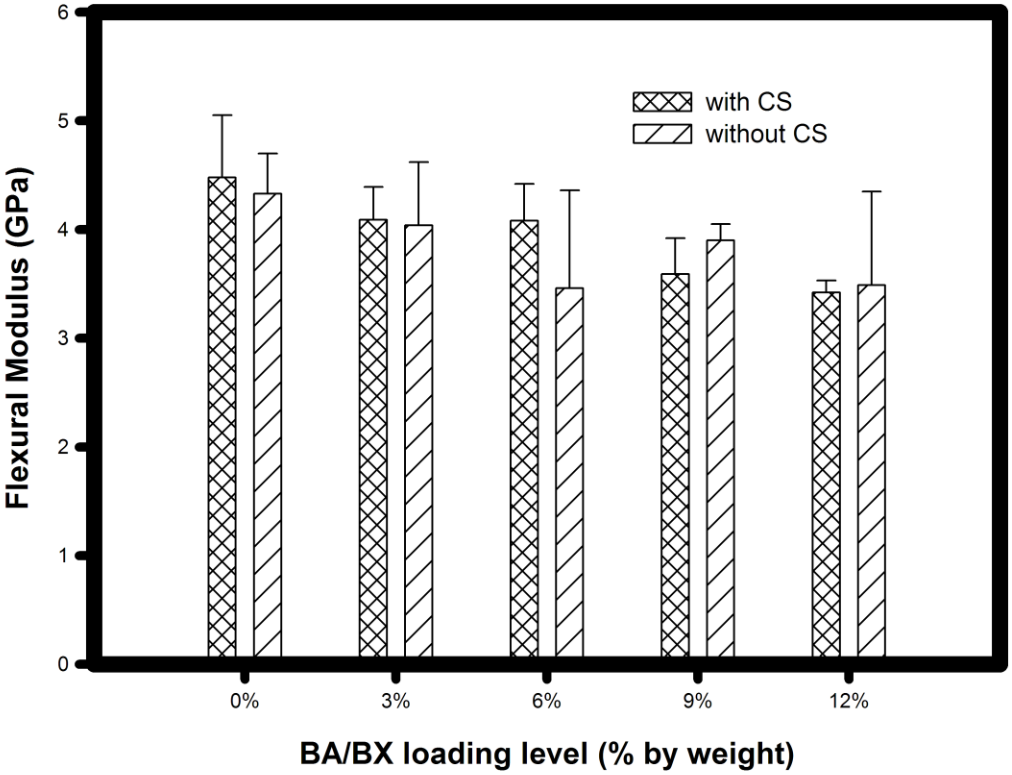

Fig. 3. Flexural modulus of WPCs with different BA/BX loadings

percentage of reduction in flexural modulus of the WPC samples was 23.66%, which occurred in the 12% BA/BX sample. Kiani *et al.* (2011) reported that the strength of wood plastic composites depends on the properties of the constituents and the interfacial interaction. The treated samples contain BA/BX compounds; therefore, their polymer content was relatively lower than that of the control samples. The BA/BX compounds also interfered with the compatibility between the wood and polymer matrix, reducing tensile strength. These results were consistent with previous studies, which found that the use of FRs resulted in weak interfacial adhesion between the matrix and/or WF, as well as the weakening of the crystalline part of the cellulose chain in WPCs (Ayrilmis *et al.* 2011; Kurt and Mengeloglu 2011; Stark *et al.* 2010). In the present study, this is attributed to weak adhesion between the polymer matrix and WF with the addition of BA/BX compounds. Figures 2 and 3 showed that flexural strength and modulus values of samples with and without CS had less variation. Baysal *et al.* (2007) also found that wood specimens pretreated with BA and BX mixture generated less MOR or MOE levels compared to that of specimens without BA and BX mixture pretreatment. Yildiz *et al.* (2004) determined the effects of wood preservatives on MOR and MOE. There were no significant differences in MOE. Yalinkilic *et al.* (1999) found that boric acid pretreatment of compressed wood polymer composite (CWPC) had no significant adverse effect on the MOE and MOR. Further work will be needed to consider the combined effect of CS, MAPE, and BA/BX to the mechanical properties of WPC by IR spectroscopy and Scanning Electron Microscope (SEM).

Fire Performance of WPCs

Heat release rate (HRR)

Combustion tests were conducted to measure the heat release rate (HRR) of the BA/BX samples. This is the basic parameter for fire modeling and denotes the rate at which heat energy is released per unit area of the sample (Xiao *et al.* 2011). Figure 4 shows the HRR of the samples, and average values for the other parameters tested are presented in Table 3B. One-way analysis of variance (ANOVA) tests in Tables 3A.

The results shown in Fig. 4 and Table 3B indicate that the BA/BX treatment provided modest improvements in fire performance for the WPCs. The BA/BX-treated samples demonstrated peak HRR reductions of 2.45%, 4.85%, 11.68%, and 17.68%, respectively, compared with the untreated samples.

From Table 3, the initial peak heat release rate (Peak HRR), average heat release rate at 60 s and 300 s (HRR-60s and HRR-300s), total heat release rate (HRR-Total), and effective heat of combustion (EHC) of the treated WPC samples were all lower than those of the untreated WPC control, and gradually decreased with increasing BA/BX content.

Compared with the Peak HRR of 330.8 kW/m^2 for the control, the lowest Peak HRR was 281.1 kW/m^2 for samples treated with 12% BA/BX—a decrease of 15.0% (Table 3). The 12% BA/BX samples also had the lowest HRR-300s at 249.7 kW/m^2, compared with 294.5 kW/m^2 for the control (Table 3). The HRR-Total for the 12% BA/BX samples was also the lowest, at 100.5 kW/m^2, compared with 116.4 kW/m^2 for the control.

The control samples also demonstrated the lowest EHC values (24.85 MJ/kg), compared with 23.88 MJ/kg for the 12% BA/BX samples.

Table 3A. ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Peak-HRR	Between Groups	4960.223	4	1240.056	735.211	0.0001
	Within Groups	16.867	10	1.687		
	Total	4977.089	14			
HRR-60s	Between Groups	2152.280	4	538.070	645.684	0.0001
	Within Groups	8.333	10	0.833		
	Total	2160.613	14	1		
HRR-300s	Between Groups	4350.567	4	087.642	1796.765	0.0001
	Within Groups	6.053	10	0.759		
	Total	4356.620	14			
HRR-Total	Between Groups	481.983	4	120.496	158.686	
	Within Groups	7.593	10	0.759		0.0001
	Total	489.576	14			
EHC	Between Groups	2.471	4	0.618	0.980	1.461
	Within Groups	6.305	10	0.630		
	Total	8.776	14			
MLR	Between Groups	3.644E-04	4	9.110E-05	21.023	0.0001
	Within Groups	4.333E-05	10	4.333E-06		
	Total	4.077E-04	14			
SEA	Between Groups	1005.865	4	251.466	685.206	0.0001
	Within Groups	3.670	10	0.367		
	Total	1009.534	14			
SPR	Between Groups	3.670	4	0.918	33.974	0.0001
	Within Groups	0.270	10	2.701E-02		
	Total	3.940	14			
Total oxygen Consumed	Between Groups	199.931	4	49.983	159.096	0.0001
	Within Groups	3.142	10	0.314		
	Total	203.072	14			

*The mean difference is significant at the 0.05 level.

Table 3B. Cone Calorimeter Results for WPCs with Different Loadings of BA/BX

BA/BX (wt. %)	Peak HRR (kW/m^2)	HRR-60s (MJ/m^2)	HRR-300s (MJ/m^2)	HRR-Total (MJ/m^2)	EHC (MJ/kg)
0%	330.89(1.55)	264.4(0.62)	294.5(0.21)	116.4(0.78)	24.85(0.98)
3%	322.9(1.33)	239.1(0.93)	277.4(0.81)	113.3(0.67)	24.81(0.99)
6%	315.5(0.65)	258.3(0.82)	261.1(0.68)	109.5(0.61)	24.56(0.14)
9%	296.2(0.73)	235.7(0.34)	251.2(0.66)	105.1(0.76)	23.99(0.31)
12%	281.1(0.70)	237.3(0.87)	249.7(0.65)	100.5(0.73)	23.88(0.23)
BA/BX (wt. %)	MLR (g/s)	SEA (m^2/kg)	SPR (kW/m^2)	Total oxygen consumed (g)	
0%	0.084(0.001)	277.88(0.76)	11.58(0.11)	74.24(0.63)	
3%	0.075(0.002)	274.57(0.40)	11.23(0.08)	72.11(0.10)	
6%	0.072(0.001)	258.55(0.52)	10.25(0.08)	69.73(0.65)	
9%	0.071(0.002)	270.76(0.40)	10.54(0.25)	66.96(0.39)	
12%	0.075(0.001)	282.75(0.22)	10.53(0.07)	63.94(0.25)	

Reported values represent means with standard deviations in parentheses based on three replicates. Initial peak heat release rate (Peak HRR, kW/m^2), heat release rates at 60 s and 300 s (HRR-60s and HRR-300 s, MJ/m^2), total heat release rate (HRR-Total, MJ/m^2), average effective heat of combustion (EHC, MJ/m^2), mass loss rate (MLR, g/s), specific extinction area (SEA, m^2/kg), total smoke production rate (SPR kW/m^2), and total oxygen consumed (g) were measured as a function of time (between 37 s and 530 s).

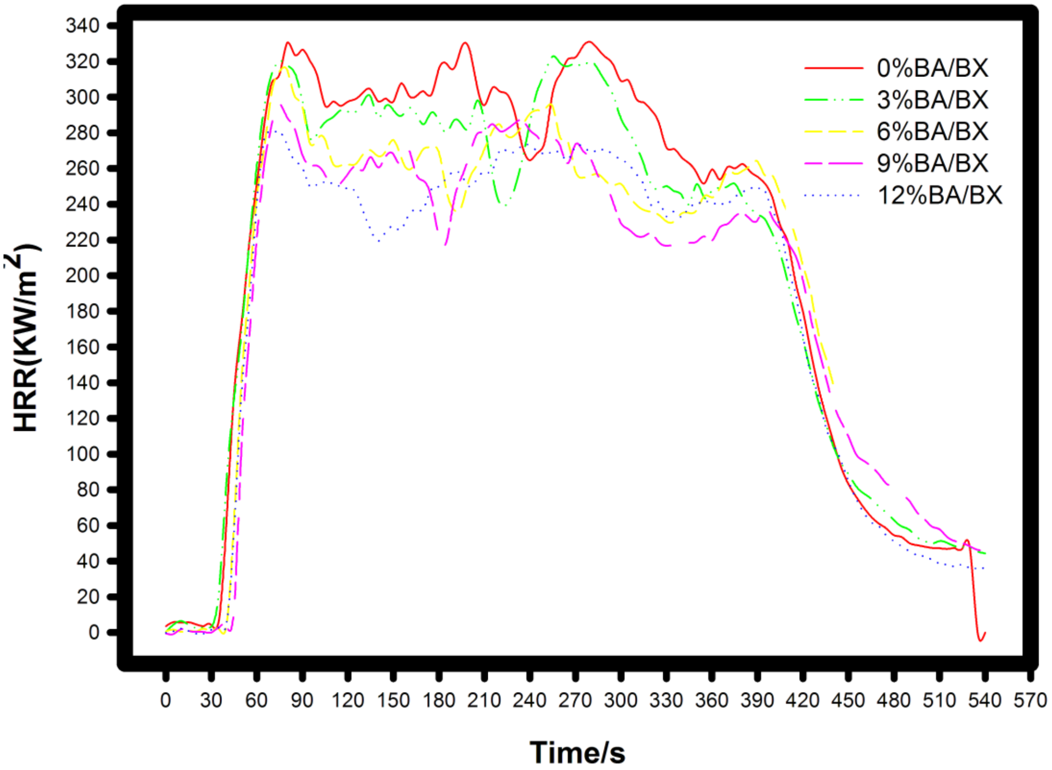

Fig. 4. Curves of heat release rates (HRR kW/m^2) plotted over time for the WPC control sample and samples containing 3%, 6%, 9%, and 12% of BA/BX by weight

In general, HRR was diminished by the addition of BA/BX compounds, which can be attributed to two main factors. First, adding BA/BX diluted the volatile decomposition compounds of the WPC with non-volatile compounds. Overall, this diminished the proportion of volatiles in the WPCs and therefore decreased HRR. Second, differences in BA can promote ethanol dehydration, which can generate large amounts of carbon when the borate and cellulose undergo thermal decomposition. This difference is, again, caused by the alteration of the proportion of the BA/BX compounds within the matrix material. Reductions in Peak HRR and HRR-Total in the BA/BX samples can be attributed to the formation of a protective, glass-like covering on the WPC surface during combustion, which obstructed oxygen access and thus prevented complete combustion (Xiao *et al*. 2011).

Time to ignition (TTI)

In the present study, time to ignition (TTI) was a measure of the time it took for the WPC surface to reach the critical ignition temperature during combustion tests. This depended on the thermal inertia of the material (a product of heat capacity, thermal conductivity, and density), which changed as a result of incorporating fillers (Hull *et al.* 2011). The 9% BA/BX samples (TTI, 44 s) demonstrated an 18.9% increase in TTI compared with the control (TTI, 37 s; Fig. 5). However, BA/BX compounds only had a slight effect on TTI. Fang *et al.* (2013) reported that in contrast with WF–PVC, ZB only had a slight effect on TTI and av-HRR of WF–PVC but had a higher pk-HRR, which is unfavorable to fire retardancy. Babrauskas (2003) found some models correlating TTI and heat flux have also been proposed assuming no changes in the physical constants of the material prior to ignition. Thomson and Drysdale (1987) observed that generally, for non-charring polymers in radiative heating, it is assumed that TTI is independent of the imposed heat flux. This is due to the lack of considerations such as melting/decomposition of the polymer during heating and others including changes in the surface absorption/emission properties (affecting the heat flux). Thus, there is always uncertainty in predicting the TTI. Some studies have confirmed that in polymer nanocomposites, TTI exhibits completely unpredictable and variable trends relative to neat polymers (Laoutid *et al.* 2009; Morgan 2006; Kiliaris and Papaspyrides 2010; Levchik 2010).

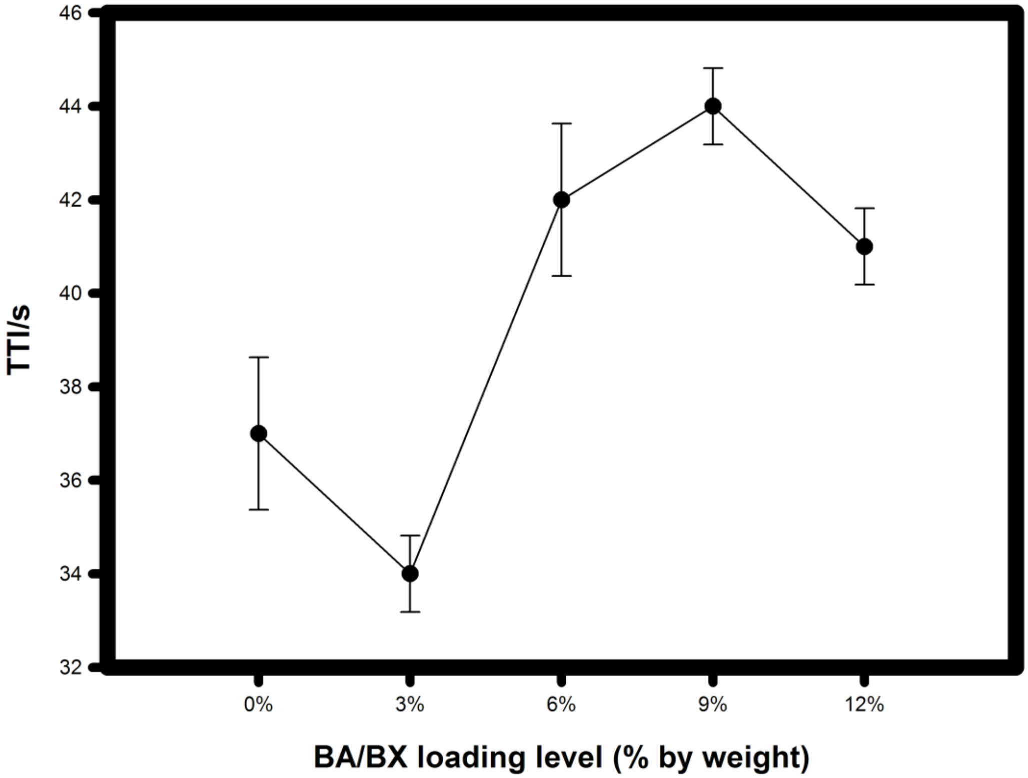

Fig. 5. Time to ignition (TTI) for WPCs with different BA/BX loadings

As the BA/BX melted during combustion, it formed a vitreous outer layer along the WF fibers, which isolated them from oxygen and heat transmission. The cellulose hydroxylation and the condensed-phase boron reacted and formed BA ester, which inhibited the formation of levoglucosan and reduced the amount of combustible gas. Because BA promotes ethanol dehydration, large amounts of carbon were generated when the borate and cellulose underwent thermal decomposition. These results indicated that the addition of BA/BX compounds to WPCs can improve FR performance.

Mass loss rate (MLR)

Mass loss rate (MLR) is a measure of a sample’s mass loss per unit of time during combustion. It reflects the material’s thermal degradation, volatility, and flaming degree given a measured amount of fire strength. In the present study, as BA/BX content increased from 0% to 12%, MLR gradually decreased (Fig. 6 and Table 3). The reported thermal properties supported this (Table 4 and Fig. 7 TGA curves for WPCs with different BA/BX loadings).

The present results demonstrated that BA/BX compounds in the WPCs accelerated char formation. Therefore, the decreases in MLR seen in these tests were likely caused by the formation of a protective layer of compact black char, which prevented gas penetration into the WPC and caused incomplete combustion. Baysal *et al.* (2004 and 2007) found that BA and BX mixture pretreatment played an important role in reducing weight losses of wood, and weight losses of BA and BX mixture pretreated WPC were reduced than those of monomer only treated wood clarifying the protective effect of boron in combustion. Baysal *et al.* (2002) and Yalinkilic *et al.* (1998) found that the weight loss of untreated and boron–vinyl monomer combination-treated wood. This indicated that the wood became more difficult to ignite and more oxygen was needed to burn the treated materials, consistent with the effect of boron (Le *et al*. 1990).

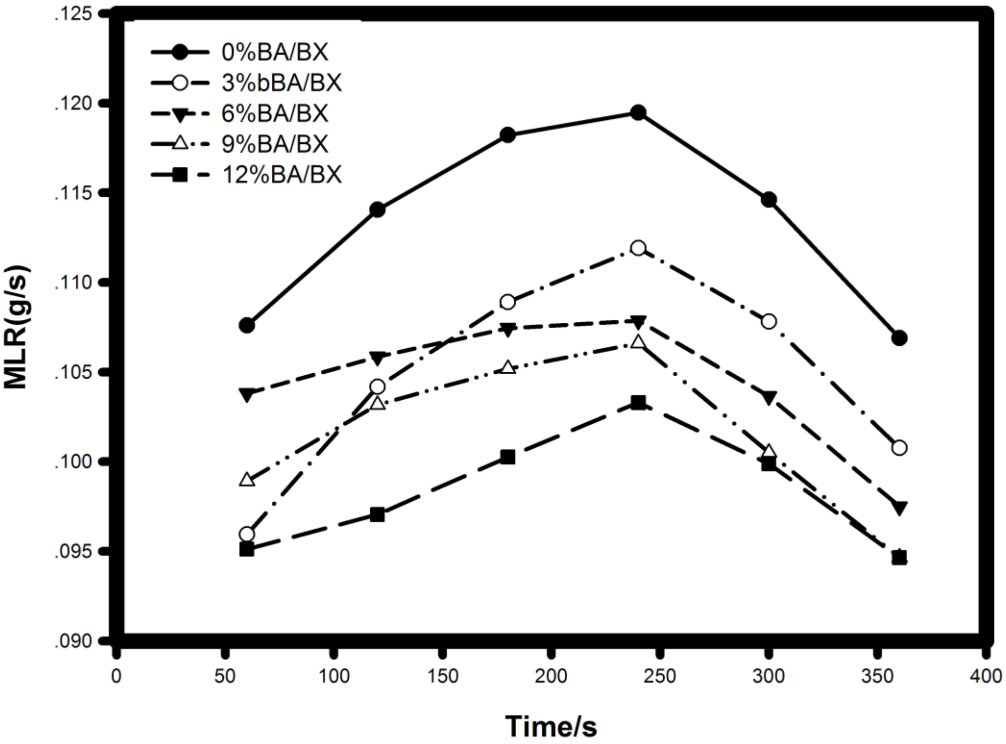

Fig. 6. Mass loss rate (MLR) of WPCs with different BA/BX loadings

Smoke production rate (SPR)

Smoke production rate is defined as the rate at which smoke is produced during combustion per unit of time. During a fire, inhalation of smoke can be one of the greatest hazards to life; therefore, understanding smoke production by WPCs during combustion is critical to improving their fire safety (Anthony 1999). Table 3 shows that SPR values of the BA/BX-treated WPC samples were lower than those of the untreated controls. The 12% BA/BX samples with the lowest SPR of 10.53 kW/m^2 exhibited a 9.97% decrease in SPR, compared with 11.58 kW/m^2 for the untreated control samples. This can be attributed to the presence of BA/BX compounds, which altered the proportion of volatiles, increased char formation, and led to a decrease in SPR. Thus, this study supports the idea that char formation is a mechanism of smoke suppression (Starnes *et al*. 2003).

Thermal degradation

Thermogravimetric analysis results (curves of TGA and DTG) of samples A, B_1, B_2, B_3, and B_4 in pure nitrogen atmosphere are shown in Figs. 7 and 8, and the calculated typical data are listed in Table 4.

Table 4. Thermogravimetric Analysis Data under Pure Nitrogen

Samples	T_{initial} (°C)	First stage			Second stage			Residue at 600 °C (%)
		Temperature range (%)	T_{max} (°C)	Mass loss(%)	Temperature range (%)	T_{max} (°C)	Mass loss(%)	
A	208	208-401	358	24.8	401-498	476	73.1	11.35
B_1	209	209-401	335	28.1	401-498	474	68.4	15.35
B_2	209	209-401	333	25.9	401-497	475	67.6	15.86
B_3	210	210-402	331	32.8	402-498	475	64.7	18.48
B_4	237	237-411	329	22.9	411-498	473	61.9	22.42

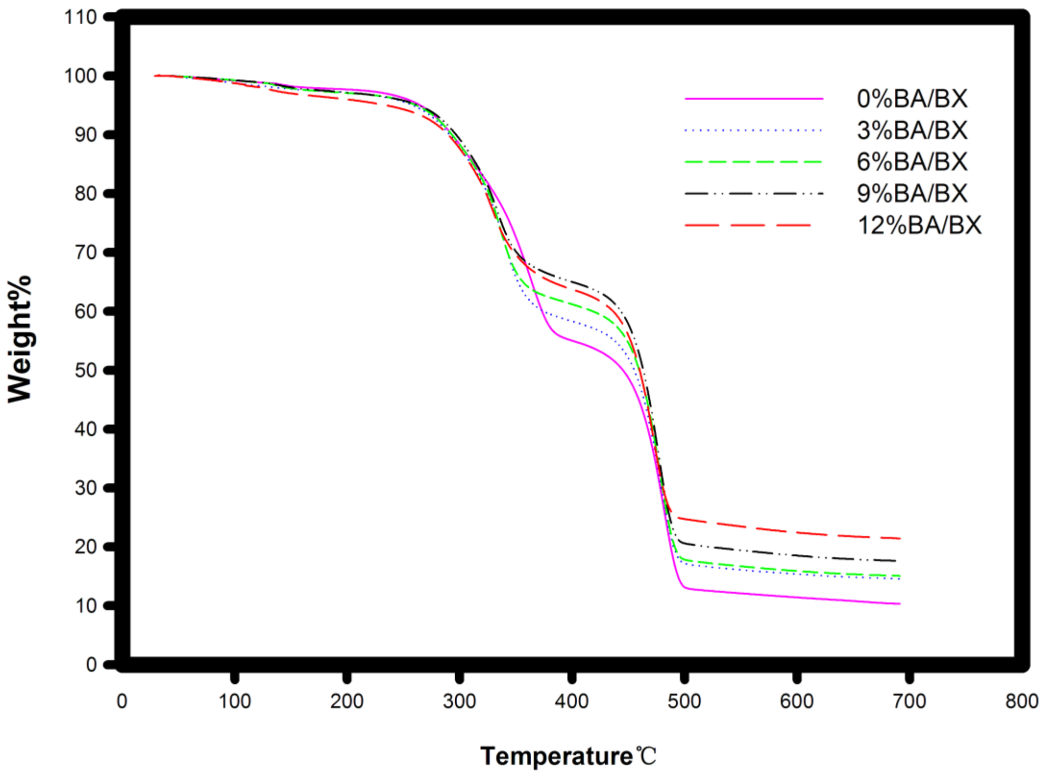

Fig. 7. TGA curves for WPCs with different BA/BX loadings

The TGA curves in Fig. 7 showed that the specimens underwent a two-step thermal degradation processes. In the first step, thermal degradation of wood flour took place, and the thermal degradation of HDPE in WF/HDPE/CS composites took place mainly at the second step. A similar phenomenon has been reported by others (Yemele *et al*. 2010; Bouza *et al*. 2009; Meng and Tjong 1999). Shen *et al.* (2008) found such effects for boric acid and boron oxide (B_2O_3). B_2O_3 softens at 350 °C and flows above 500 °C, leading to the formation of a protective vitreous layer. Studies by Fang *et al.* (2013) and Bai *et al.* (2011) indicated that the thermal degradation temperature scope of wood-flour is from 201 °C to 410 °C. From their DTG curves in Fig. 8, it is apparent that when the BA/BX compounds were added, the decomposition temperature of wood flour and HDPE shifted to lower and higher temperature, respectively. According to the data of Table 5, addition of the BA/BX compounds made the thermal degradation of the WF/HDPE/CS composites system take place earlier and promoted char formation. BA/BX compounds hardly affected the initial decomposition temperature of WF/HDPE/CS composites while it reduced the T_{max} in the first stage. However the residues were increased; residue of 3%, 6%, 9%, and 12% BA/BX samples at 600 °C increased by about 35.2%, 39.7%, 62.8%, and 97.4%, respectively, more than that of 0% BA/BX samples.

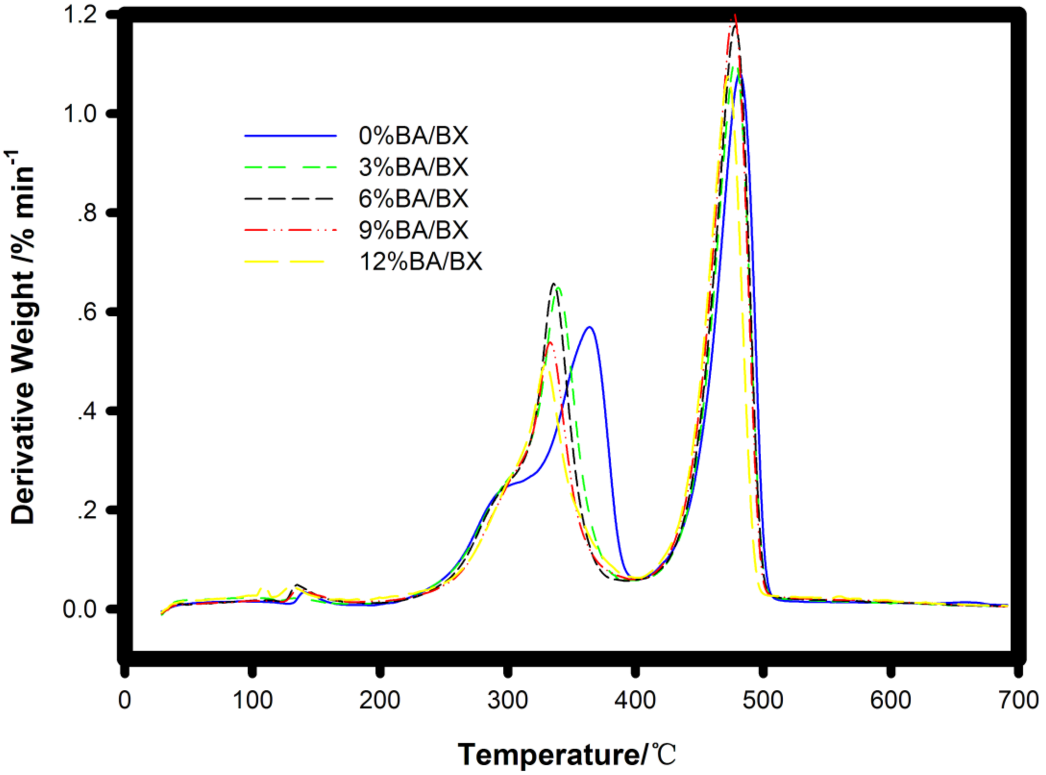

Fig. 8. DTG curves for WPCs with different BA/BX loadings

Figure 6 shows the mass loss rate (MLR) of WPCs with different BA/BX loadings. These results indicate that the BA/BX compounds gave improved thermal properties at high temperature and could enhance the formation of the char. Stark *et al.* (2011) indicated that 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. In the process, the boron helps block oxygen from the surface and slows the escape of gases. Wang *et al.* (2004) reported that the boron residue also reacts with hydroxyl groups of the wood components (cellulose, hemicelluloses) to generate additional quantities of water and form an inorganic char, which acts as an insulator that slows down the rate of composite degradation. This has been confirmed by other work (Ning and Guo 2000; Shen *et al*. 2008; Yildiz *et al*. 2009). The thermal degradation of WF-PE-CS composites is a complex process, which can be attributed to the interaction between PE and wood/CS.

Mechanisms for the effects of BA/BX compounds on thermal decomposition of WPC composites were further confirmed by FTIR–ATR.

Decay Resistance

One-way analysis of variance (ANOVA) tests indicated that the weight loss percentage of white rot fungus ($P < 0.005$), and the weight loss percentage of brown rot fungus ($P < 0.0001$) of the WPCs significantly decreased with the addition of BA/BX except 6% BA/BX (Tables 5A and 5B).

Table 5. Means with Standard Error and Results of ANOVA for the weight loss percentage of WPCs with Different Weight Percentages of BA/BX

Table 5A. ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
White rot fungus	Between Groups	10.708	4	2.677	7.322	0.005
	Within Groups	3.655	10	0.366		
	Total	14.364	14			
Brown rot fungus	Between Groups	27.982	4	6.955	866.811	0.0001
	Within Groups	8.070E-02	10	8.070E-03		
	Total	28.062	14			
*The mean difference is significant at the 0.05 level.						

Table 5B. Means and Standard Error of the weight loss percentage

Composite Code	White rot fungus	Brown rot fungus
	Weight loss percentage (%)	Weight loss percentage (%)
A	5.17 (0.142)a	6.22 (0.078)a
B_1	4.86 (0.045)ac	5.18 (0.074)a
B_2	5.45(1.089)a	6.30 (0.111)bc
B_3	3.76 (0.093)bc	3.20(0.026)b
B_4	3.26 (0.142)b	3.27(0.054) bc
Means with different letters for each property are significantly different at the 0.05 level of Within Groups.		

Weight loss is an important parameter for assessing decay of solid wood (Lomelí-Ramírez *et al.* 2009); for this reason the discussion will only focus on the percentage of weight loss. The average weight loss percentages of samples A, B_1, B_2, B_3, and B_4 after brown and white rot fungus decay tested for 12 weeks are given in Table 5B. Figure 9 shows that the average weight loss percentages of samples with CS WPC decreased with increasing BA/BX content, except for 6% BA/BX. There were no significant differences with the brown and white rot fungus decay tested. For the white rot fungus decay tested, compared with the control, the average weight loss percentage of the 9% and 12% BA/BX WPC samples decreased by 27.3% and 36.9%, respectively, and for the brown rot fungus decay tested, the results were 48.6% and 47.4%, respectively. Usually weight losses below 10% have been reported in most studies of WPCs exposed to fungal attack. For example Clemons and Ibach (2002) reported weight losses approaching 6% for 3 mm thick WPCs made with pine and HDPE. Pendleton *et al.* (2002) reported weight losses from 4% to 8% in specimens made of 70% maple, 24% HDPE, and 6% processing additives. Mankowski and Morrell (2000) reported weight losses of nearly 16% for WPCs made of 70% wood and 30% HDPE exposed to *P. placenta*, and about 20%

weight loss for those exposed to *G. trabeum*. Baysal *et al* (2007) found that monomer treatment caused higher weight losses when compared to mixture treated. Yalinkilic *et al.* (1999) tested decay resistance of compressed wood polymer composites (CWPC) pretreated with boric acid. Decay test results showed that boric acid pretreated CWPC has remarkably good resistance to fungal attack. But pretreatment with a boric acid and borax mixture imparted further resistance to WPC so that it became nearly totally resistant to both test fungi. The remarkably good decay resistance of WPC can be explained by its high moisture exclusion efficiency and inhibition of mycelial spread (Yalinkilic *et al.* 1991). The characterization of decay resistance of this family of WPC presented in this paper is the first part of a comprehensive study of these composites. In particular, scanning electron microscopy analysis and surface chemistry of decayed WPC will be presented in subsequent papers.

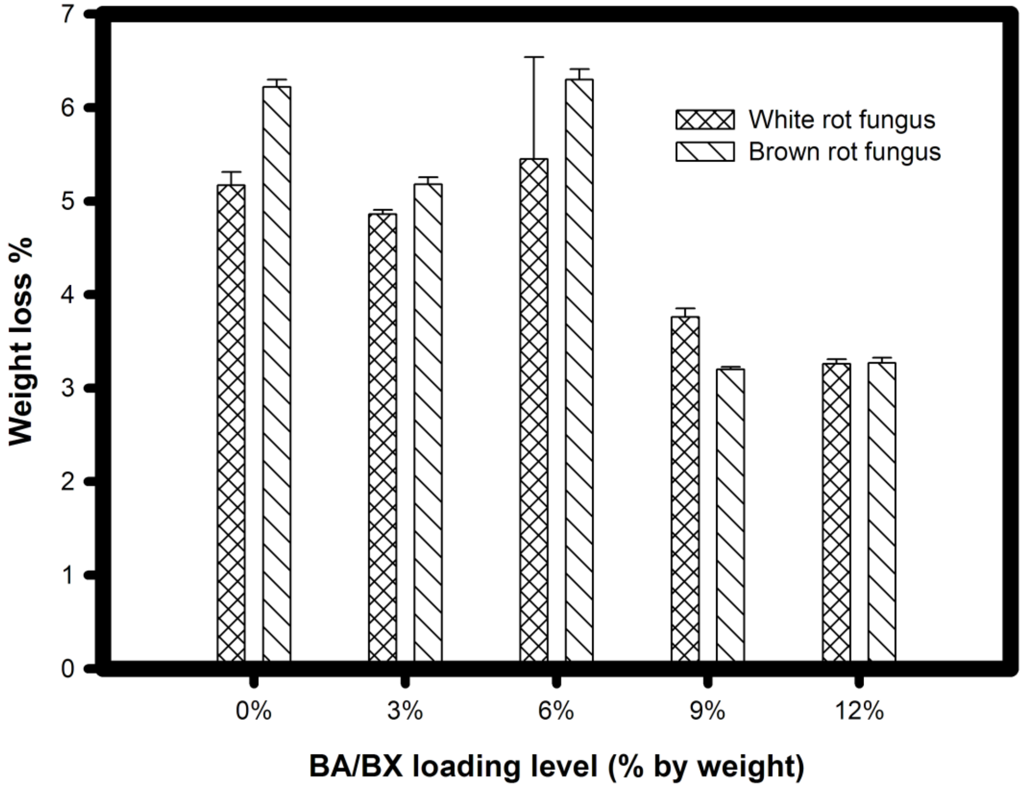

Fig. 9. Weight loss percentage for WPCs with different BA/BX loadings

CONCLUSIONS

1. The tensile strength, flexural strength, and flexural modulus of the WPC samples with 6% chitosan (CS) decreased when the boric acid/borax (BA/BX) content was increased from 3% to 12% by weight. The tensile strength, flexural strength, and flexural modulus of WPC samples without CS first increased and then decreased with increasing BA/BX content from 3% to 12% by weight. The mechanical properties showed no significant differences when comparing specimens without CS and specimens with 6% CS. The results showed that additive BA/BX compounds could

degrade the mechanical properties of wood-plastic composites (WPC). This may likely be attributable to poor compatibility between the wood fiber and polymer matrix due to the increased surface contamination of the wood surface by the presence of loosely adhering crystalline deposits of the boron compounds. Another reason could be due to involvement of the boron compounds in the esterification reactions between wood flour and the coupling agent MAPE.

2. Cone calorimeter tests indicated that the fire-related parameters HRR, Peak HRR, HRR-60s and HRR-300s, HRR-Total, EHC, and SPR all decreased with increasing BA/BX content. The TTI increased with increasing BA/BX content, from 3% to 9%. These results suggest that adding BA/BX compounds to WPCs can modestly improve fire performance. This can be attributed to wood becoming more difficult to ignite and more oxygen being needed to burn the treated materials as consistent to the effect of BA/BX compounds, which are understood to form a protective layer of compact black char. The TGA and DTG results showed that addition of BA/BX compounds made the thermal degradation of WF/HDPE/CS composites system take place earlier and promoted char formation. Also the residues of 3%, 6%, 9%, and 12% BA/BX samples at 600 ^{o}C were increased by about 35.2%, 39.7%, 62.8%, and 97.4%, respectively, in comparison to the 0%BA/BX samples. These results indicated that the BA/BX compounds gave improved thermal properties at high temperature and could enhance the formation of the char.
3. The average weight loss percentages of samples A, B1, B2, B3, and B4 after brown and white rot fungus decay tested for 12 weeks were investigated. When white and brown rot fungus decay was tested, compared with the control, the average weight loss percentage of the 9% and 12% BA/BX WPC samples decreased by 27.3%, 36.9%, and 48.6%, 47.4%, respectively. The results showed that BA/BX compounds could enhance decay resistance of WPC. This may be attributed to its high moisture exclusion efficiency and inhibition of mycelial spreading.

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