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Effect of boron and phosphate compounds on physical, mechanical, and fire properties of wood–polypropylene composites

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ABSTRACT

Physical, mechanical, and fire properties of the injection-molded wood flour/polypropylene composites incorporated with different contents of boron compounds; borax/boric acid and zinc borate, and phosphate compounds; mono and diammonium phosphates were investigated. The effect of the coupling agent content, maleic anhydride-grafted polypropylene, on the properties of the composites with fire-retardant was also investigated. The composites with the zinc borate had the highest dimensional stability and strength in the bending, tensile, and izod impact, followed by the monoammonium phosphate, borax/boric acid, and diammonium phosphate treatments. The treatments produced modest improvements in fire performance as indicated by reductions in the heat release rates. Best results were achieved with the phosphate treatments. The Scanning Electron Microscope–Energy Dispersive Spectroscopy elemental mapping of the samples revealed that the outer surface of the wood fibers was coated by some crystalline deposits of the fire-retardants.

1. Introduction

Wood–plastic composites (WPCs) represent an emerging class of materials that combines favorable performance and cost attributes of both wood and thermoplastics. Lignocellulosics are increasingly applied for reinforcement in thermoplastics such as polypropylene and polyethylene due to wood's low density, good thermal insulation and mechanical properties, reduced tool wear, unlimited availability, low price, and problem-free disposal [1]. Wood flour is the most common lignocellulosic used in WPCs. It is a commercially available material sourced from industrial residues such as planer shavings, sawdust, and wood chips and ground to a consistent mesh size. WPCs are stiffer, exhibit less creep, and are more dimensionally stable than unfilled plastic lumber.

Current growth rate of the WPC market is 22% for North America and 51% for Europe [2]. Decking for outdoor applications represent the largest market for WPCs both in North America and Europe and in both regions growth is most rapid in the decking segment [3]. WPC market share in the European decking sector is estimated to be around 6%. In Europe, total WPC production amounts to 120 thousand tons (excluding product destined for the auto industry). Around 68 thousand tons of this production is currently destined for the decking sector. The positive growth in WPC decking has led manufacturers to introduce residential construction applications include siding, roofing, windows, door frames, and outdoor furniture. Further expansion into the residential construction industry and development of applications for the furniture industry require an understanding of the fire performance of the WPCs. As organic materials, i.e. both polymers and wood, are sensitive to fire, improvement of fire retardancy of the composite materials has become important in order to comply with the safety requirements of the WPC products. Polymers employed in WPCs, burn and drip in case of fire leading to a very risky scenario. Thus, FR agents must be employed in order to improve fire behavior. The fire performance of WPCs is not well understood, and there is little information regarding the effectiveness of various FRs in the public domain.

Even though a lot of work has been reported on the fire properties of thermoplastics [4–7], effect of FRs on the technological and fire properties of the wood flour reinforced thermoplastic composites only now is being more extensively investigated. The primary objective of this study was to determine effects of the boron

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compounds and phosphate compounds on the physical, mechanical, and fire properties of the injection molded WPCs with and without a coupling agent. The physical properties of natural fiber/polyolefin composites can be greatly enhanced by a coupling agent [8]. There is no any study related to effects of coupling agent content on the physical, mechanical, and fire properties of the WPC with FRs. The secondary objective was to investigate effect of the coupling agent content on the properties of the WPCs with FRs.

2. Materials and methods

2.1. Materials

Wood particles were obtained from beech (*Fagus orientalis* Lipsky) lumbers by using laboratory type disk chipper with three knives. The moisture content of the wood particles, as determined by oven-dry weight, was found to be 40–50% prior to the treatment. The wood particles were ground in a laboratory *Wiley* grinder. The wood flour passing through a US 35-mesh screen was retained by a US 80-mesh. The wood flour was dried in a laboratory oven at 102 °C for 24-h to a moisture content of 0–1% based on the oven-dry weight of wood and then stored in a polyethylene bag.

The polypropylene (PP) (MFI/230 °C/2.16 kg = 5 g/10 min) produced by Petkim Petrochemical Co., Turkey, was used as the polymeric material. Maleic anhydride-grafted PP (MAPP-Optim-425, MFI/190 °C/2.16 kg = 120 g/10 min) was supplied by Pluss Polymers Pvt. Ltd. in India.

Four FR systems (powder) were investigated:

1. A mixture of boric acid (BA) (H_3BO_3) (ρ = 1.7 g/cm^3) and borax (BX) ($Na_2B_4O_7{\cdot}10H_2O$) (ρ = 1.4 g/cm^3) (BA/BX, 1:1 by weight).
2. Zinc borate (ZB) ($3ZnO{\cdot}2B_2O_3$) (ρ = 2.8 g/cm^3).
3. Monoammonium phosphate (MAP) $NH_4H_2PO_4$ (ρ = 1.8 g/cm^3).
4. Diammonium phosphate (DAP) $(NH_4)_2HPO_4$ (ρ = 1.6 g/cm^3).

2.2. Preparation of injection molded WPC specimens

The wood flour, PP and MAPP granulates, and the FR powder were processed in a 30-mm co-rotating twin-screw extruder with a length-to-diameter (L/D) ratio of 30:1. The barrel temperatures of the extruder were controlled at 170, 180, 185, and 190 °C for zones 1, 2, 3, and 4, respectively. The temperature of the extruder die was held at 200 °C. The extruded strand passed through a water bath and was subsequently pelletized. These pellets were stored in a sealed container and then dried to the moisture content of 1–2% before the injection molding. The temperature used for injection molded specimens was 180–200 °C from feed zone to die zone. The WPC specimens were injected at injection pressure between 45 and 50 kg/m^2 with cooling time about 30 s. Finally, the specimens were conditioned at a temperature of 23 °C and relative humidity (RH) of 50% according to ASTM D 618 [9]. Air-dry density values of the specimens varied from 1010 to 1070 kg/m^3. The raw material formulations used for the WPCs are presented in Table 1.

Table 1
Compositions of the injection molded WPC formulations.

WPC formulation[a]	WPC compositon (wt.%)			
	FR content	MAPP content	Wood flour	Polypropylene
Control	–	–	40	60
BX/BA	4	–	38	58
ZB	4	–	38	58
MAP	4	–	38	58
DAP	4	–	38	58
BX/BA	8	–	36	56
ZB	8	–	36	56
MAP	8	–	36	56
DAP	8	–	36	56
BX/BA	12	–	34	54
ZB	12	–	34	54
MAP	12	–	34	54
DAP	12	–	34	54
BX/BA	4	2	37	57
ZB	4	2	37	57
MAP	4	2	37	57
DAP	4	2	37	57
BX/BA	8	4	34	54
ZB	8	4	34	54
MAP	8	4	34	54
DAP	8	4	34	54
BX/BA	12	6	31	51
ZB	12	6	31	51
MAP	12	6	31	51
DAP	12	6	31	51

[a] BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate. FR: fire retardant. MAPP: maleic anhydride-grafted polypropylene.

2.3. Determination of physical properties

The thickness swelling (TS) and water absorption (WA) tests after 2-h of boiling in water were carried out according to ASTM D 570 [10] specifications. The test specimens were in the form of a disk 50.8 mm in diameter and 3.2 mm in thickness. The conditioned specimens were entirely immersed for 2-h in a container of boiling distilled water. At the end of the immersion time, the specimens were taken out from the water and all surface water was removed with a clean dry cloth. The specimens were weighed to the nearest 0.01 g and measured to the nearest 0.001 mm immediately. Ten replicate specimens were tested for each WPC formulation.

2.4. Determination of mechanical properties

The flexural properties of the specimens with dimensions of 127 mm × 12.7 mm × 3.2 (thickness) mm, modulus of rupture (MOR) and modulus of elasticity (MOE), were measured in three-point bending tests using a standard material testing system (Zwick Roel Z010) at a crosshead speed of 2.8 mm/min in accordance with ASTM D 790 [11]. Tensile strength of the specimens (dogbone shape (type III)) were tested with a crosshead speed of 5 mm/min in accordance with ASTM D 638 [12] using a Zwick Roel Z010. Five replicate specimens were tested for the tensile and flexural properties of each WPC formulation. The izod pendulum impact strength (notched) were performed according to ASTM D 256 [13] using a Zwick Roel HIT5.5P impact testing machine. Ten replicate specimens were tested for the izod pendulum impact strength of each WPC formulation.

2.5. Fire performance

Heat release measurements in the cone calorimeter were conducted in accordance with ASTM E 1354 [14]. The US Forest Products Laboratory cone calorimeter used for these tests was a Model No Cone 2A, Combustion Analysis System (Auto-Cal) manufactured by Atlas Electric Devices Company of Chicago, IL. Specimens were 100 mm × 100 mm and specimen thickness was 10 mm. Specimens were conditioned at 23 °C and 50% RH prior to the testing. The cone calorimeter tests were conducted in the horizontal orientation with the conical radiant electric heater set at a heat flux level of 50 kW/m^2. The specimens were tested in the optional retainer frame but without the wire grid over the test specimen. Ignitability was determined by using a 4 s criteria for sustained ignition for observing the time for sustained ignition of the specimen. Two replicate specimens were tested for each type of specimen.

2.6. Statistical analysis

An analysis of variance, ANOVA, was conducted ($p < 0.01$) to evaluate the effects of the FR and MAPP contents on the physical and mechanical properties of the WPCs. Significant differences among the average values of the WPC types were determined using Duncan's multiple range test. Regression analysis of the cone calorimeter results as function of the treatment levels was conducted to determine the statistical significance of the changes in results due to the FR treatments.

3. Results and discussion

3.1. Physical properties

The TS and WA values of the untreated and FR-treated WPC specimens without the coupling agent (MAPP) are presented in Table 2. As compared with the control specimens, the water resistance of the uncoupled specimens significantly decreased with increasing the FR content. However, the water resistance improved with the addition of the coupling agent and when the MAPP and the corresponding FR contents were increased from 2 to 4 wt.% and 4 to 8 wt.%, respectively (Table 3). The significant differences for the uncoupled and coupled specimens with the FR are shown by letters in Tables 2 and 3, respectively. Among the treatment

Table 2
Physical and mechanical properties of the un-coupled WPCs with FR.

WPC formulation[a]	FR content (wt.%)	MAPP content (wt.%)	Physical properties			Mechanical properties			
			Density (kg/m^3)	Thickness swelling (%)	Water absorption (%)	Modulus of rupture (MPa)	Modulus of elasticity (MPa)	Tensile strength (MPa)	Notched impact strength (J/m)
				2-h boiling water immersion					
Control	–	–	1030 (20)	1.31 (0.06) a[b]	1.60 (0.10) a	68.8 (6.9) a	8610 (150) a	26.3 (0.6) a	25.7 (1.7) a
BX/BA	4	–	1050 (15)	1.48 (0.07) ab	1.83 (0.10) bd	64.2 (8.0) bc	8845 (261) ab	24.8 (0.7) abd	23.9 (2.7) bc
ZB	4	–	1010 (20)	1.40 (0.07) ab	1.74 (0.15) abc	65.6 (7.7) ab	8915 (344) ab	25.4 (2.2) ab	24.6 (2.5) ab
DAP	4	–	1010 (15)	1.49 (0.09) ab	1.88 (0.15) cd	63.2 (4.8) bd	8745 (233) ab	24.2 (1.1) bd	23.4 (1.9) bc
MAP	4	–	1020 (20)	1.44 (0.10) ab	1.80 (0.13) bc	64.9 (6.5) bc	8865 (295) ab	25.0 (0.8) abd	24.1 (1.5) abc
BX/BA	8	–	1060 (20)	1.67 (0.10) cd	1.98 (0.12) de	62.5 (6.9) cd	9004 (336) bc	23.2 (0.1) cde	22.5 (1.9) cd
ZB	8	–	1040 (30)	1.51 (0.09) bd	1.86 (0.17) bd	64.2 (9.4) bc	9245 (158) cd	24.7 (0.7) abc	22.8 (1.3) bcd
DAP	8	–	1050 (20)	1.72 (0.10) c	2.06 (0.12) eg	61.4 (7.34) bde	8904 (413) ab	22.9 (0.6) de	21.3 (2.1) de
MAP	8	–	1060 (30)	1.65 (0.13) cd	1.94 (0.08) d	63.3 (8.2) bd	9085 (202) bc	24.0 (1.0) bd	22.7 (1.4) d
BX/BA	12	–	1050 (20)	1.82 (0.11) ce	2.20 (0.24) fg	58.5 (5.72) ef	9314 (205) cd	21.6 (0.2) e	20.4 (5.2) e
ZB	12	–	1010 (10)	1.73 (0.13) c	2.05 (0.20) eg	61.0 (7.3) ed	9488 (111) d	23.5 (1.7) cd	21.6 (1.7) de
DAP	12	–	1010 (20)	1.96 (0.11) e	2.23 (0.18) g	56.6 (6.3) f	9279 (192) dc	21.8 (0.8) e	20.5 (2.3) e
MAP	12	–	1030 (10)	1.80 (0.17) ce	2.14 (0.23) g	59.2 (5.3) ef	9383 (134) d	22.0 (1.4) e	21.2 (1.4) de

[a] See Table 1 for WPC formulation. BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate. FR: fire retardant. MAPP: maleic anhydride-grafted polypropylene. The values in the parentheses are standard deviations.
[b] Groups with same letters in column indicate that there is no statistical difference ($p < 0.01$) between the samples according Duncan's multiply range test.

Table 3
Physical and mechanical properties of the coupled WPCs with FR.

WPC formulation[a]	FR content (wt.%)	MAPP content (wt.%)	Physical properties			Mechanical properties			
			Density (kg/m^3)	Thickness swelling (%)	Water absorption (%)	Modulus of rupture (MPa)	Modulus of elasticity (MPa)	Tensile strength (MPa)	Notched impact strength (J/m)
				2-h boiling water immersion					
BX/BA	4	2	1060 (10)	1.24 (0.05) a[b]	1.48 (0.14) ab	70.3 (5.6) ac	9085 (124) ab	27.0 (0.5) a	26.2 (1.3) ab
ZB	4	2	1040 (30)	1.14 (0.06) abd	1.30 (0.17) ac	69.5 (7.3) abc	9288 (321) a	28.8 (3.2) ab	26.9 (1.0) ab
DAP	4	2	1040 (10)	1.26 (0.13) a	1.52 (0.09) b	67.4 (4.4) b	8905 (103) b	27.3 (1.8) a	25.7 (1.8) a
MAP	4	2	1020 (30)	1.19 (0.15) ab	1.37 (0.21) abc	68.2 (5.9) ab	9159 (287) ab	27.8 (1.5) a	26.4 (2.3) ab
BX/BA	8	4	1020 (25)	1.04 (0.10) bc	1.24 (0.10) cd	71.8 (6.5) cde	9376 (281) ad	28.8 (0.7) ab	27.8 (1.4) bc
ZB	8	4	1050 (10)	0.93 (0.06) c	1.13 (0.09) d	73.6 (7.1) d	9784 (159) c	30.6 (0.7) b	29.3 (2.1) c
DAP	8	4	1050 (25)	1.07 (0.08) bc	1.33 (0.16) ac	70.7 (6.1) ade	9356 (310) ad	28.4 (1.3) ac	27.4 (2.0) b
MAP	8	4	1010 (10)	0.96 (0.07) cd	1.19 (0.10) cd	72.0 (5.5) de	9652 (215) cd	29.6 (1.2) b	28.4 (1.6) c
BX/BA	12	6	1070 (30)	1.17 (0.09) ab	1.35 (0.11) ac	69.7 (6.1) abe	9557 (267) cd	28.1 (0.2) ac	27.2 (1.8) bc
ZB	12	6	1050 (20)	1.06 (0.05) abc	1.22 (0.08) cd	72.2 (5.6) de	9844 (314) c	29.5 (1.6) bc	28.8 (1.9) c
DAP	12	6	1060 (30)	1.20 (0.14) ab	1.44 (0.11) ab	68.6 (7.0) ab	9482 (266) d	27.7 (1.3) a	26.5 (2.2) ab
MAP	12	6	1040 (20)	1.13 (0.09) abd	1.26 (0.14) cd	70.0 (4.8) abe	9753 (303) cd	28.6 (0.9) ab	27.9 (2.0) bc

[a] See Table 1 for WPC formulation. BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate. FR: fire retardant. MAPP: maleic anhydride-grafted polypropylene. The values in the parentheses are standard deviations.
[b] Groups with same letters in column indicate that there is no statistical difference ($p < 0.01$) between the samples according Duncan's multiply range test.

groups, the specimens with the ZB had the highest water resistance, followed by the MAP, BX/BA, and DAP treatments, respectively. For example, when the ZB or DAP contents increased to 12 wt.%, the average and WA values of the uncoupled specimens increased to 2.05% and 2.23%, respectively. Wood treated with the inorganic FRs is usually more hygroscopic than untreated wood [15]. A similar result was found for the WPCs with the FRs in this study. The TS and WA values of the uncoupled specimens with the FRs at higher contents were always higher than lower contents.

The TS and WA of the specimens were significantly affected by the FR type and content. This was mainly attributed to the different volume percentages of the FRs. The volume percentages of the particle-based materials such as wood flour and FR powder are affected by their densities because the volume percentage increases with decreasing particle density. As a result, the volume percentages of the FRs were different from each other due to the different densities of the FRs. The ZB has the lowest volume percentage at all the treatment levels, followed by the MAP, BX/BA, and DAP, because it has the highest density value among the FRs. The severity of the contamination of the wood surface increase with increasing volumetric percentage of the FRs. The contamination of the wood surface by the FRs resulted in a poor compatibility between the wood and polymer matrix surfaces (Fig. 1). The poor compatibility allows for easier moisture intrusion compared with the WPCs without the FRs. For this reason, the TS and WA values of the uncoupled specimens increased with increasing FR content.

Although the TS and WA values of the uncoupled specimens were adversely affected by the FRs, they decreased with the addition of the MAPP (Table 3). This result was expected for two reasons: (1) the reduction in the wood flour replaced by the coupling agent and (2) because the strong interfacial bonding caused by the coupling agent increased the water resistance of the WPCs with the FRs. The WA values of the coupled specimens were lower than those of the uncoupled specimens at all treatment levels. For example, The TS and WA values of the uncoupled specimens with 12 wt.% ZB were 1.73% and 2.05% while they were 1.06% and 1.22% for the coupled (6 wt.% MAPP) specimens with 12% ZB, respectively. The MAPP plays an important role in improving compatibility and adhesion between polar wood and non-polar polymer matrix by forming bridges of chemical bonds between the

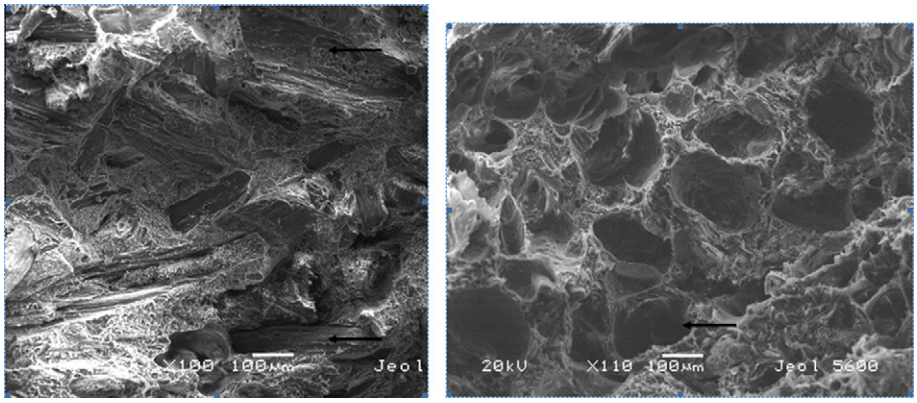

Fig. 1. Poor compatibility between the wood fiber and polymer matrix of the un-coupled WPC specimen containing 8% by weight of fire-retardant (The SEM photos from the failure surface of the tensile strength specimen).

fiber and the matrix (Fig. 2). The anhydride groups in the MAPP enter into an esterification reaction with the surface hydroxyl groups of wood fibers and covalently bond to the hydroxyl groups [16]. Hydrogen-bonding sites for water molecules decrease with decreasing hydroxyl groups on the wood surface as a function of the contamination of the wood surface by the FRs. This resulted in lower TS and WA values for the coupled WPCs with the FRs.

The water resistance of the WPCs increased when the contents of the MAPP and FR increased to 4 wt.% and 8 wt.%, respectively. However, the water resistance of the WPCs decreased when the MAPP and FR contents increased from 4 to 6 wt.% and 8 to 12 wt.%, respectively. This can be explained by the reduction in the wood flour content and the decreasing interfacial bonding between the functional polar groups of the wood and MAPP due to increasing volume percentage of the FR powder. The results of TS and WA showed 6 wt.% MAPP could not suppress the negative effect of 12 wt.% FR on the compatibility between wood fiber and polymer due to a high contamination of the wood surface by the crystalline deposits of the FR (Fig. 1).

3.2. Mechanical properties

3.2.1. Flexural properties

The MOR of the uncoupled specimens decreased with increasing the FR content while the MOE increased. The uncoupled control specimens had the highest MOR, followed by the uncoupled specimens with the ZB, MAP, BX/BA, and DAP, respectively (Table 2). The MOE of the uncoupled or coupled specimens significantly improved with increasing the FR content. This finding was consistent with previous studies [6,7]. The significant differences are shown by letters in Tables 2 and 3. The flexural performance of the coupled WPCs with the FR were better than the uncoupled WPCs with the FRs, as expected. The negative effect of the FRs (up to 8 wt.%) on the interface compatibility between the wood and the polymer was prevented by using the MAPP (up to 4 wt.%). For example, the MOR of the uncoupled specimens with 8 wt.% ZB were 64.2 N/mm^2 while it was 73.6 N/mm^2 for the specimens with 8 wt.% ZB and 4 wt.% MAPP. However, a further increment in the ZB content (12 wt.%) decreased the MOR (72.2 N/mm^2) of the coupled specimens (6 wt.% MAPP). The results indicated that the negative effect of 12 wt.% FR on the MOR of the specimens could not suppressed by increasing the MAPP content up to 6 wt.%. Although the interface bonding was negatively affected by the boron compounds, the MOR of the 6 wt.% coupled specimens containing 12 wt.% the FR was higher than those of the 2 wt.% coupled specimens containing 4 wt.% the FR (Table 3).

3.2.2. Tensile strength

The tensile strength of the uncoupled specimens decreased with increasing the FR content. For example, as compared with the control specimens, the tensile strength values of the uncoupled specimens with the 12 wt.% BX/BA or 12 wt.% ZB decreased by 18% and 11% as a function of increasing the FR content, respectively. The decrease in the tensile strength of filled plastics with addition of FRs was reported in previous studies [5,17,18]. The compatibility between the wood and PP was decreased by adding the FRs (Fig. 1). However, the interfacial action between the wood and PP improved with the incorporation of the MAPP (Fig. 2). The visual evaluation of the failure surface of the tensile strength specimens with the FR using the Scanning Electron Microscope–Energy Dispersive Spectroscopy (SEM–EDS) elemental mapping of the samples revealed that outer surface of the wood fibers was coated by some

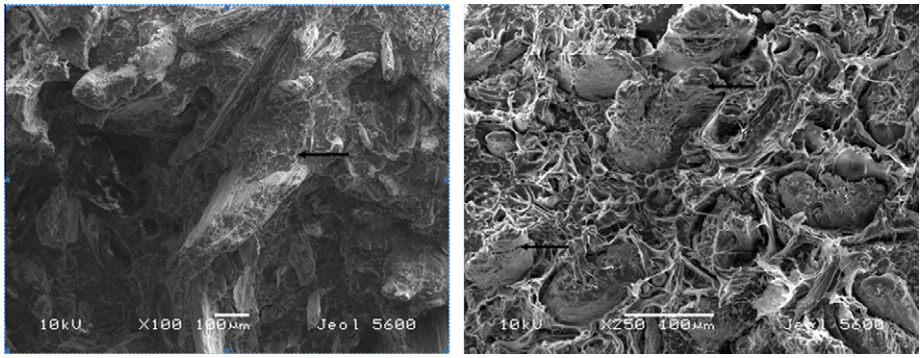

Fig. 2. Strong compatibility between the wood fiber and polymer matrix of the 4 wt.% MAPP coupled WPC specimen containing 8% by weight of fire-retardant (The SEM photos from the failure surface of the tensile strength specimen).

crystalline deposits of the FRs, thereby increasing surface area of the solids within the WPC and reducing the bonding efficiency of the polymer (Fig. 3). This resulted in the contamination of the wood surface by the presence of loosely adhering crystalline deposits of the FRs, which caused the poor compatibility between the wood and polymer matrix. The different volumetric percentages of the ZB and BX/BA in the WPC had a significant effect on the tensile strength of the specimens. The interface bonding between the wood and polymer matrix was adversely affected by an increase in the volumetric content of the FRs. The specimens with the ZB had the highest tensile strength because the ZB had the lowest volume percentage among the FR types at all loading levels.

The interface bonding between the polar wood and non-polar polymer matrix improved with increasing the MAPP content up to 4 wt.%, as shown in the SEM micrographs of the tensile fracture surface of WPCs with the 8 wt.% FR (Fig. 2). Incorporation of the MAPP into the WPC improved interfacial adhesion between wood and polymer of the specimens with the FRs. By closely examining these micrographs, it can be observed that wood is strongly bonded to the polymer and therefore wood fiber breakage occurs. The decrease in the polymer matrix content of the WPC as a function of the increase in the FRs content is also responsible for the low tensile strength because when the FR content in the WPC increases, the amount of the plastic as the adhesive, decreases. These findings were consistent with previous studies [6,7].

3.2.3. Impact strength

The uncoupled specimens with the FR showed lower notched impact strength compared with the untreated control specimens (Table 2). For example, when the contents of the BX/BA or ZB increased to 12 wt.%, the impact strength of the uncoupled specimens decreased to 21% and 16%, respectively. This was mainly attributed to the poor compatibility between the wood and polymer matrix due to the crystalline deposits of the FRs (Fig. 3). The specimens with the ZB had the highest impact strength, followed by the MAP, BX/BA, and DAP treatments. The impact resistance of the specimens improved when the FR and MAPP contents increased up to 8 wt.% and 4 wt.%, respectively. However, a further increase in the MAPP content (6 wt.%) could not suppress the negative effect of the FRs at the content of 12 wt.% on the impact strength of the specimens. A similar effect was also observed for the MOR and tensile properties of the specimens.

3.3. Fire properties

The cone calorimeter results for the WPC formulations are presented in Table 4. In the cone calorimeter tests; the heat release rate, mass loss rate, and specific extinction area were measured as a function of time. The observation of time for sustained ignition (TSI, s) was also recorded. From the curves of heat release rate, the recorded observations included the initial peak heat release rate (PHRR, kW/m^2) and the heat release rates averaged over 300 s (AHRR-300, kW/m^2) after sustained ignition. The average effective heat of combustion (AEHOC, MJ/kg) was calculated from the total heat released and the total mass loss. The mass loss rate data was averaged for the duration of 10–90% of the ultimate mass loss (AMLR). Obscuration of a laser beam in the exhaust duct was recorded as a measure of the visible smoke development from the burning specimen. Average specific extinction area (ASEA, m^2/kg) was computed from smoke obscuration data for duration of the test.

The results (Table 4) indicated that the treatments provided modest improvements in the fire performance. The results presented in Table 4 are means and standard deviations for the two replicates. The specimens with the longest average TSI (24.5 s) were the ones treated with 4% MAP and 2% MAPP compared with 19.3 s for the untreated 40 wt.% wood flour/60 wt.% PP control specimens. The FR treated specimens demonstrated some reductions in the heat release rate (Fig. 4). Compared with the PHRR of 535 kW/m^2 for the untreated WPC controls, the lowest PHRR was 416 kW/m^2 for the specimens treated with 4 wt.% MAP and 2 wt.% MAPP. The same specimens also had the lowest AHRR-300 at 248 kW/m^2 compared with 377 kW/m^2 for the untreated WPC controls. Compared with 10.8 g/m^2 s for the untreated WPC controls, the AMLR for the specimens treated with 4 wt.% MAP and 2 wt.% MAPP was also the lowest at 6.2 g/m^2 s. The specimens with the lowest AEHOC values were the untreated WPC control specimens (30.3 MJ/kg) compared with 34.1 MJ/kg for the 8 wt.% BX/BA plus 4 wt.% MAPP specimens. Compared with the ASEA of 468 m^2/kg for the untreated WPC controls, the 12 wt.% BX/BA without MAPP specimens had the lowest ASEA at 436 m^2/kg and the 8% DAP without MAPP specimens had the highest ASEA at 759 m^2/kg.

The PHRR results for the four treatments without the coupling agent are illustrated in Fig. 5. The results for the AEHOC showed either no effect or higher AEHOC with treatment level. One mechanism for an effective FR treatment is to reduce the AEHOC. In earlier studies, the addition of the fire-retardant or the replacement of

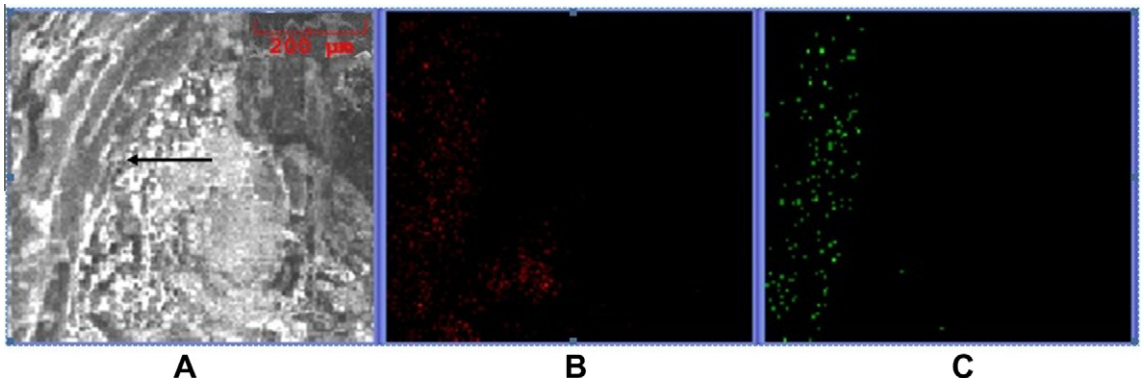

Fig. 3. Typical elementary chemical analysis using a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) of the failure surface of the tensile strength specimen without MAPP after the failure. The SEM/EDS micrographs show that the outer surface of the wood fibers was coated by some crystalline deposits of the boron compounds. This result in the poor compatibility (the arrow's way on the SEM micrograph, (A)) between the wood fiber and polymer matrix. The EDS micrographs: red color (B) shows the element Boron (B) and green color (C) shows the element Zinc (Zn). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Cone calorimeter results for the WPCs with different loading levels of FR and coupling agent.

WPC formulation[a]	FR content (wt.%)	MAPP content (wt.%)	Time to sustained ignition (s)	Peak heat release rate (kW/m^2)	Avg. heat release rate 300 s (kW/m^2)	Total heat released (MJ/m^2)	Avg. mass loss rate (10–90%) (g/m^2 s)	Avg. effective heat of combustion (MJ/kg)	Avg. specific extinction area (m^2/kg)
Control	–	–	19.3 (4.0)	535 (19)	377 (1)	319 (1)	10.8 (0.4)	30.3 (0.7)	468 (21)
BX/BA	4	–	19.8 (0.1)	513 (17)	371 (14)	245 (103)	12.7 (2.9)	31.9 (1.1)	472 (64)
ZB	4	–	20.2 (1.5)	530 (11)	403 (12)	335 (14)	11.1 (0.6)	32.7 (0.8)	514 (101)
DAP	4	–	19.6 (1.9)	499 (21)	345 (28)	308 (2)	9.0 (1.2)	33.0 (0.2)	508 (39)
MAP	4	–	17.2 (0.7)	543 (10)	336 (19)	318 (20)	8.4 (0)	33.9 (1.7)	658 (79)
BX/BA	8	–	20.7 (0.8)	510 (10)	384 (18)	323 (2)	10.1 (0.8)	33.4 (0.04)	508 (21)
ZB	8	–	21.2 (2.3)	479 (18)	342 (16)	311 (10)	9.2 (1.0)	31.7 (0.8)	480 (102)
DAP	8	–	18.6 (0.4)	495 (20)	315 (40)	299 (12)	8.9 (1.1)	31.9 (0.8)	759 (15)
MAP	8	–	19.5 (0.6)	470 (3)	293 (16)	300 (1)	7.9 (0.1)	32.2 (0.01)	636 (43)
BX/BA	12	–	20.9 (0.3)	504 (11)	364 (6)	295 (4)	9.6 (0.8)	33.0 (0.7)	436 (42)
ZB	12	–	20.2 (0.6)	474 (20)	334 (12)	315 (12)	9.0 (0.1)	33.2 (0.4)	477 (51)
DAP	12	–	20.4 (1.1)	455 (2)	303 (11)	286 (7)	7.8 (0.1)	31.3 (0.8)	598 (270)
MAP	12	–	20.9 (1.4)	434 (18)	268 (11)	288 (4)	6.9 (0.3)	30.7 (0.4)	573 (89)
BX/BA	4	2	20.1 (0.5)	465 (4)	382 (25)	318 (1)	10.9 (0.3)	33.0 (1.5)	474 (8)
ZB	4	2	20.4 (1.5)	518 (1)	393 (35)	317 (6)	9.9 (0.8)	33.9 (1.0)	493 (76)
DAP	4	2	19.0 (1.3)	481 (18)	290 (12)	310 (6)	7.0 (0.1)	33.3 (0.4)	722 (29)
MAP	4	2	24.5 (0.7)	416 (13)	248 (13)	291 (3)	6.2 (0.1)	31.8 (0.3)	550 (86)
BX/BA	8	4	20.3 (0.3)	507 (4)	377 (13)	310 (7)	9.9 (0.3)	34.1 (0.6)	509 (69)
ZB	8	4	20.9 (0.1)	499 (20)	357 (30)	314 (5)	9.6 (0.9)	33.4 (0.6)	468 (51)
DAP	8	4	23.3 (0.3)	466 (4)	343 (23)	313 (7)	8.8 (0.7)	33.5 (0.9)	530 (103)
MAP	8	4	21.7 (0.5)	477 (13)	301 (45)	300 (14)	7.6 (0.4)	31.8 (0.5)	645 (8)
BX/BA	12	6	22.3 (0.7)	495 (15)	384 (50)	306 (15)	10.0 (0.4)	34.0 (3.4)	545 (54)
ZB	12	6	20.1 (0.3)	495 (2)	367 (29)	310 (9)	9.8 (0.5)	33.2 (0.1)	488 (10)
DAP	12	6	20.1 (0.1)	448 (23)	266 (10)	311 (8)	6.8 (0.4)	32.9 (0.2)	615 (45)
MAP	12	6	19.9 (0.3)	474 (16)	294 (20)	295 (5)	8.6 (0.6)	31.4 (0.6)	687 (98)

[a] See Table 1 for WPC formulation. BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate. MAPP: maleic anhydride-grafted polypropylene. FR: fire retardant. The values are the means and standard deviations (in the parentheses) for the two replicates.

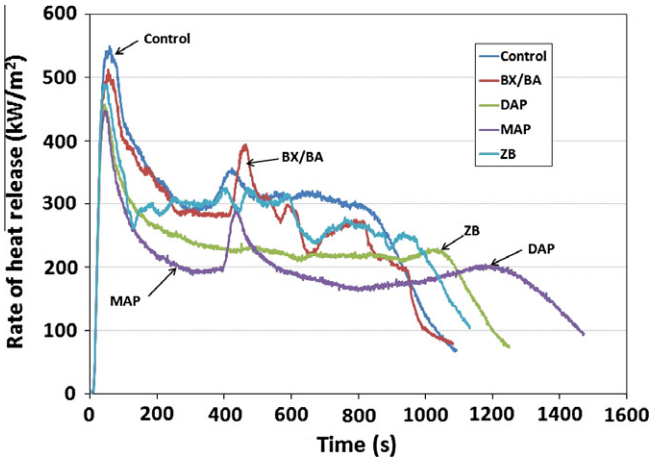

Fig. 4. Graphs of the heat release rates plotted with time for the control specimen and the four uncoupled WPC specimens containing 12% by weight of fire-retardant (one of two replicates). BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate.

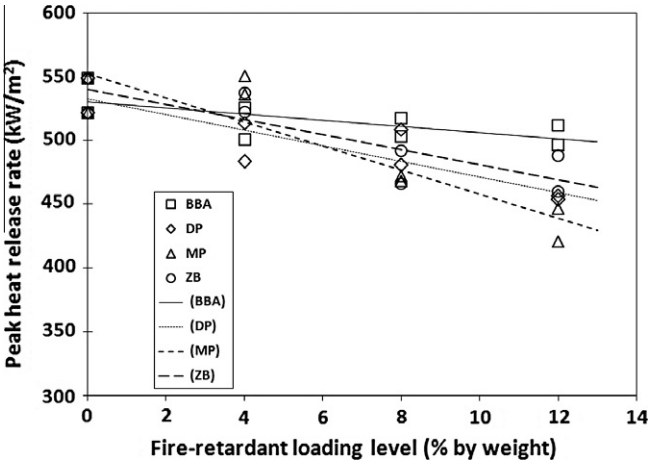

Fig. 5. Peak heat release rates for four fire-retardant treatments without coupling agent plotted against the fire-retardant treatment level. BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate.

the plastic with wood flour resulted in reductions in the AEHOC [19]. In these earlier studies, only the plastic content was reduced to accommodate the addition of the FR chemicals. The heat content of polypropylene is much higher than the heat content of wood. Another common mechanism of fire-retardant treatment is to increase the residual mass fraction and thereby reduce the production of flammable volatile gases. Except for the BX/BA without coupling agent and the MAP with coupling agent, the increase in residual mass fraction for the different treatments was similar and statistically significant according to the regression analysis.

The wood and plastic content were evenly adjusted to accommodate the 4 wt.%, 8 wt.%, and 12 wt.% addition of the FR chemical. Each FR treatment level included specimens with and without a coupling agent (the MAPP). For specimens with the coupling agent, the loading level of the coupling agent was 50 wt.% of the loading level of the FR chemical. Examination of the data indicated that the addition of the coupling agent had no consistent effect on the fire test results. The improvements for the 12 wt.% ZB over the untreated 40 wt.% wood flour and 60 wt.% PP were not as great as in the earlier studies in which the wood flour was 50 wt.% and

the ZB content was 10 wt.% [4,7,19]. In the earlier studies, the addition of FR chemical reduced the polymer content only, whereas in the current study, the addition of FR chemical was accommodated by equal reductions in wood and polymer contents. Thus, the improved results for the ZB in the two earlier studies reflected the added reductions in the polymer content. Further investigation is needed to determine whether any processing factors affected the effectiveness of the chemical treatments.

4. Conclusions

The following general conclusions can be drawn from the study provided in the paper:

1. Compared with the control WPCs, incorporation of the boron and phosphate compounds and the corresponding reduction in the wood flour content decreased the water resistance and mechanical properties of the uncoupled WPCs, except for the MOE. The WPCs with ZB had the highest water resistance and mechanical properties followed by the MAP, BX/BA, and DAP treatments.
2. The use of the coupling agent (up to 4 wt.%) improved the water resistance and mechanical properties of the WPCs with the FR (up to 8 wt.%). However, the water resistance and strength of the WPCs decreased when the MAPP and FR contents increased from 4 to 6 wt.% and 8 to 12 wt.%, respectively. The result showed that an increment in the MAPP content (6 wt.%) did not prevent the negative effect of the FRs (12 wt.%) due to a high contamination area of the wood surface by the crystalline deposits of the FRs. In general, the dimensional stability and mechanical properties of the 6 wt.% coupled specimens containing 12 wt.% the FR were better than those of the 2 wt.% coupled specimens containing 4 wt.% the FR.
3. The SEM–EDS elemental mapping of the samples revealed that outer surface of the wood fibers was coated by some crystalline deposits of the FRs. This resulted in the poor compatibility between the wood and polymer matrix in the WPCs.
4. The FR treatments produced modest improvements in fire performance as indicated by reductions in the heat release rates. The results from the cone calorimeter tests indicated that the phosphate treatments provided more improvements in the fire performance than the boron treatments. It is noted that in this study, the increased FR treatments was accommodated by reducing the percentage wood flour as well as the percentage PP. Reducing both the wood fiber content and the polymer content equally to accommodate the addition of the FR chemicals likely reduced the net improvement provided by the FR treatment. There was no evidence that the coupling agent affected the results.
5. Based on the findings obtained in the present study, a 4/8 wt.% formulation of the MAPP and FR appears to a practical choice for the WPCs having optimum physical and mechanical properties.

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