

# Properties of Flat-Pressed Wood Plastic Composites Containing Fire Retardants

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**ABSTRACT:** This study investigated physical, mechanical, and fire properties of the flat-pressed wood plastic composites (WPCs) incorporated with various fire retardants (FRs) [5 or 15% by weight (wt)] at 50 wt % of the wood flour (WF). The WPC panels were made from dry-blended WF, polypropylene (PP) with maleic anhydride-grafted PP (2 wt %), and FR powder formulations using a conventional flat-pressing process under laboratory conditions. The water resistance and strength values of the WPC panels were negatively affected by increasing the FR content as compared to the WPC panels without FR. The WPC panels incorporated with zinc borate (ZB) gave an

overall best performance in both water resistance and strength values followed by the panels containing magnesium hydroxide (MH) and ammonium polyphosphate (APP). For these three FR's, the best fire resistance as measured in the cone calorimeter was obtained with the 15 wt % APP treatment and then followed by 15 wt % ZB, or 15 wt % MH formulations. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3201–3210, 2011

**Key words:** cone calorimetry; fire retardant; heat release rate; hot press molding; polypropylene; strength; water resistance; wood plastic composite; WPC panel

## INTRODUCTION

The use of conventional wood-based panels, such as particleboard and medium density fiberboard (MDF), is quite limited for exterior and moist applications, due to the strong tendency of such materials to absorb water. By contrast, wood plastic composites (WPCs) show a considerably reduced affinity towards water, compared to conventional wood-based panels, what is caused by their relatively high thermoplastic content. WPCs represent a growing class of materials used by the residential construction industry and the furniture industry. Further expansion into the residential construction industry and development of applications for the furniture

industry require an understanding of the fire resistance of flat-pressed WPCs.

Fire retardants (FRs) for plastics and WPCs are completely different from those of wood materials.<sup>1</sup> Wood is typically impregnated with solutions of FRs, commonly salts, such as monoammonium (MAP) and diammonium phosphate (DAP), ammonium sulfate, zinc chloride, sodium tetraborate, boric acid, and guanylurea phosphate.<sup>2–5</sup> In plastics and WPCs, however, FRs are added as solids directly into the formulation. Hence, FRs for plastics and WPCs should be temperature resistant, in order not to be decomposed during processing. The compounds which have been found to be most effective in producing flame retardance are compounds containing bromine, chlorine, or phosphorous, or two or more of these elements. Other elements that have exhibited some flame retardant effect are antimony, boron, nitrogen, silicon, and zinc. These elements are often used with phosphorous or halogenated compounds.<sup>6</sup> Depending on the nature of the FRs, they can act chemically or physically in the solid, liquid, or gas phase. For example, halogenated compounds are said to function primarily by a vapor phase fire inhibiting mechanism through radical reaction while phosphorous compounds reduce the formation of

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TABLE I  
Compositions of the WPC Panel Formulations

WPC panel formulation	WPC panel composition								Total volume Volume (%)	Total weight Weight (%)	Total porosity (%)
	FR		WF		PP		MAPP				
	Volume (%)	Weight (%)	Volume (%)	Weight (%)	Volume (%)	Weight (%)	Volume (%)	Weight (%)			
WF-40	0	0	24.6	40	60.0	58	1.8	2	86.4	100	13.6
WF-50	0	0	30.8	50	42.2	48	1.8	2	74.8	100	25.2
WF-60	0	0	36.9	60	33.4	38	1.8	2	72.1	100	27.9
WF-70	0	0	43.1	70	24.6	28	1.8	2	69.5	100	30.5
WF-ZB	1.4	5	30.8	50	37.8	43	1.8	2	71.8	100	28.2
WF-MH	1.7	5	30.8	50	37.8	43	1.8	2	72.1	100	27.9
WF-APP	2.1	5	30.8	50	37.8	43	1.8	2	72.5	100	27.5
WF-ZB	4.3	15	30.8	50	29.0	33	1.8	2	65.9	100	34.1
WF-MH	5.0	15	30.8	50	29.0	33	1.8	2	66.6	100	33.4
WF-APP	6.3	15	30.8	50	29.0	33	1.8	2	67.9	100	32.1

APP, ammonium polyphosphate; FR, fire retardant; MAPP, maleic anhydride-grafted PP; MH, magnesium hydroxide; PP, polypropylene; WF, wood-flour; ZB, zinc borate.

flammable carbon containing gases by increasing the conversion of polymeric materials to a char residue during pyrolysis.<sup>7</sup>

Polyolefins, the other usual polymers employed in WPCs, burn and drip in case of fire leading to a very risky scenario. Thus, FR agents must be employed to improve WPC fire behavior. Various studies have been carried out on the use of FRs in WPC composites reinforced by natural fillers.<sup>6–10</sup> In these studies, the WPCs containing FRs were made by using extrusion or injection molding methods. Another possibility, which has only little been explored, is to produce fire resistant WPCs on a flat-press by using dry blend method.<sup>11</sup> Recently, Ayrimis et al.<sup>12</sup> investigated fire resistance of WPC panels made from dry blended wood flour (WF), polypropylene (PP), and FR powder (10 wt %). They have focused on one FR loading. The objective of this study was to determine the effects of changing the loading of various FRs (5 or 15% by wt) on the physical, mechanical, and fire properties of the WPC panels made using dry-blend method. In this study, cone calorimeter test was used to characterize the fire resistance of the WPC panels containing FRs, and compared the results with the WPC panels without FR.

## EXPERIMENTAL

### Materials

Commercial softwood WF (Jeluxyl WEHO 500V) used to produce WPC was obtained from a manufacturer (JELU-WERK) of WF located in Rosenberg, Germany. The WF was then dried in a laboratory oven at 102°C for 24 h to moisture content of 0–1% based on the oven-dry WF weight. PP powder (Moplen HP500V) ( $T_m = 163^\circ\text{C}$ ,  $\rho = 0.91 \text{ g/cm}^3$ , MFI/230°C/2.16 kg =

120 g/10 min) produced by Basell Polyolefine GmbH (LyondellBasell Industries, Wesseling, Germany), was used as the polymeric material. Maleic anhydride-grafted PP (MAPP) ( $\rho = 0.90 \text{ g/cm}^3$ , Scona TP PP 8112 FA) powder was supplied by Kometra (Schkopau, Germany). Significant criteria in choosing of the investigated chemicals were (a) minimum risk to human health, (b) minimum risk to environment, (c) maximum effectiveness for fire retardancy, (d) easy-supply, and (e) low-cost. The chemicals used in the experiments were found to be safe even under the worst-case exposure assumptions by NAS.<sup>13</sup>

Three FR systems (powder) were investigated:

1. Ammonium polyphosphate (APP;  $\text{NH}_4\text{PO}_3$ ) [Exolit AP, 422,  $\rho = 1.9 \text{ g/cm}^3$ , Clariant (Frankfurt, Germany)].
2. Magnesium hydroxide, [MH;  $\text{Mg}(\text{OH})_2$ ] [Apy-mag 80S,  $\rho = 2.4 \text{ g/cm}^3$ , Nabaltec AG (Schwandorf, Germany)].
3. Zinc borate (ZB;  $3\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ ),  $\rho = 2.8 \text{ g/cm}^3$  [Balmumcu Chemical, (Istanbul, Turkey)]

The WPC panels incorporated with 5 or 15 wt % of the FR system had a WF content of 50 wt %. It was also produced WPC panels without FRs at 40, 50, 60, and 70 wt % WF content levels to compare with the panels containing FRs. Table I shows the raw material formulations used for the WPC panels.

### Manufacturing process of flat-pressed WPCs

Flat-pressed WPCs were manufactured using standardized procedures that simulated industrial production at the laboratory. After mixing WF, PP, MAPP, and FR powder, the mixture was placed in a rotary drum blender. Following the blending

treatment for about 10 min, the mixture was weighed and then formed into a mat on an aluminum caul plate, using a  $450 \times 450 \text{ mm}^2$  forming frame. Wax paper was used to avoid direct contact of the PP powder with the metal platens during heating and pressing. The mats were then subjected to hot pressing, using a computer-controlled press. The maximum press pressure, pressing temperature, and total press cycle were  $45 \text{ N/cm}^2$ ,  $210^\circ\text{C}$ , and 500 s, respectively. At the end of the hot pressing cycle, the panel was moved from the hot press into a press at room temperature for cooling. The resulting WPC panels were allowed to cool for 1 week in the climate room having 65% relative humidity (RH) and  $20^\circ\text{C}$  before they were cut into test samples. Ten mm thick panels were then trimmed to a final size of  $420 \times 420 \text{ mm}^2$ . Thirty experimental WPC panels, three for each type of panel, were manufactured. The average density value of the WPC panels was  $800 \text{ kg/m}^3$ .

### Fire resistance

Heat release measurements were conducted in accordance with ASTM E 1354.<sup>14</sup> Three replicate samples were tested for each type of specimen. The samples were  $100 \times 100 \text{ mm}^2$  and sample thickness was 10 mm. The samples were conditioned at  $23^\circ\text{C}$  and 50% RH prior to testing. The cone calorimeter tests were conducted in the horizontal orientation with the conical radiant electric heater set at a heat flux level of  $50 \text{ kW/m}^2$ . 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.

### Determination of water resistance

The water resistance of the WPC samples, thickness swelling (TS) and water absorption (WA), was evaluated according to EN 317.<sup>15</sup> Eighteen samples with dimensions of  $50 \times 50 \times 10 \text{ mm}^3$  were used for each type of panel to determine the TS and WA. The samples conditioned at  $20^\circ\text{C}$  and 65% RH were placed in a container of water maintained at a temperature of  $20^\circ\text{C}$ . The weights and thicknesses of the samples were measured at different time intervals during the long period of immersion. At the end of 1, 7, 28, 56, and 112 days of submersion, the samples were removed from the water, all surface water were wiped off with a dry cloth, and weighed to the nearest 0.001 g and measured to the nearest 0.001 mm immediately. The sample thickness was determined by taking a measurement at a specific location, the diagonal crosspoint, on the sample. Density of the samples was evaluated according to the test method specified in EN 323.<sup>16</sup>

Conversion between the weight percentages and volume percentages in the WPCs was done by the eq. (1):

$$V_x = (W_x \rho_c / \rho_x) \quad (1)$$

where  $V$  is volume percentage,  $W$  is weight percentage,  $\rho$  is density, the subscript  $c$  is the WPC, and the subscript  $x$  is one of the constituents of the WPC.

### Determination of mechanical properties

The flexural properties of the samples conditioned at  $20^\circ\text{C}$  and 65% RH, modulus of rupture (MOR) and modulus of elasticity (MOE), were conducted according to EN 310.<sup>17</sup> Fifteen samples with dimensions of  $250 \times 50 \times 10 \text{ mm}^3$  were used for each type of panel to determine the flexural properties. The samples were tested on a Zwick testing system equipped with a load cell with a capacity of 50 kN. The MOR test was conducted in accordance with the third point loading method at a span-to-depth ratio of 20 : 1. The crosshead speed was adjusted so that failure would occur within an average of  $60 \pm 10 \text{ s}$ . The internal bond (IB) tests were conducted on the samples cut from the experimental WPC panels according to EN 319.<sup>18</sup> Eighteen samples with dimensions of  $50 \times 50 \times 10 \text{ mm}^3$  were used for each type of panel to determine the IB strength.

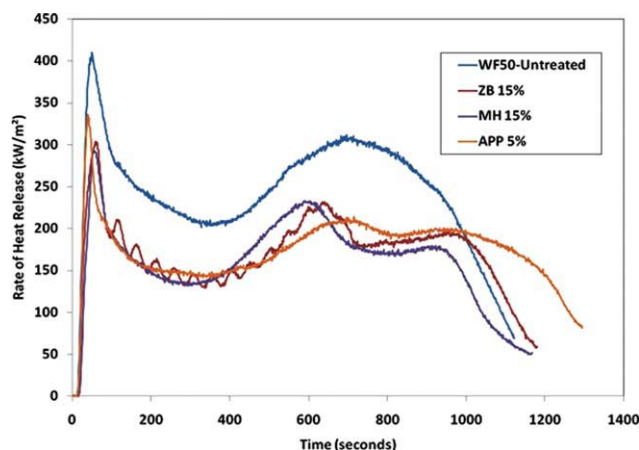
### Statistical analysis

An analysis of variance, ANOVA, was conducted ( $P < 0.01$ ) to evaluate the effect of the FR type and their loading levels on the fire, physical, and mechanical properties of the WPC panel formulations. Significant differences between the average values of the panel formulations were determined using Duncan's multiple range test.

## RESULTS AND DISCUSSION

### Fire resistance

In the cone calorimeter tests; the heat release rate (Fig. 1), mass loss rate, and specific extinction area were measured as a function of time. The heat release rate and mass loss data were used to calculate an effective heat of combustion. 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,  $\text{kW/m}^2$ ), the heat release rates averaged over 60 s (AHRR-60,  $\text{kW/m}^2$ ), 180 s (AHRR-180,  $\text{kW/m}^2$ ), and 300 s (AHRR-300,  $\text{kW/m}^2$ ) after sustained ignition. The average effective heat of combustion (AEHOC,  $\text{MJ/kg}$ ) was calculated from



**Figure 1** Examples of heat release rate curves for WF-50 untreated, WF-ZB 15%, WF-MH 15%, and WF-APP 5%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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 (AMLR10-90). 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,  $\text{m}^2/\text{kg}$ ) was computed from smoke obscuration data for duration of the test. The various results from the cone calorimeter tests for the untreated specimens and the three FR treatments evaluated for fire resistance (APP, MH, and ZB) are tabulated in Table II. As shown in Table II, the MH treatment had the lowest ASEA value. A similar result was found by Walter and Wajer.<sup>19</sup> They reported that MH acted as a flame retardant and smoke suppresser in plastics mainly by withdrawing heat from the plastic during its decomposition into magnesium oxide and water. The MH prevents oxygen to get to flammable compounds, or by forming of a protective layer and by dilution and coating. It decomposes endothermically and releases water at about 330°C, so that the flame retardant effect is based on cooling and dilution. Decomposition products insulate the plastic from heat and produce char that impedes the flow of potentially flammable gases to the flame.

Of three FR treatments, the MH had the most impact on the times for sustained ignition. Compared with the 23.8 s mean time for the 50 wt % WF untreated specimens (WF-50), the 5% treatment of MH increased the mean time to 28.2 s, and the 15 wt % treatment increased the mean time to 30.4 s (Table II). The mean times for the 15 wt % ZB (27.2 s) and 15 wt % APP (27.8 s) treatments were slightly less than the mean time for the 5 wt % MH (28.2 s). In a similar study, Stark et al.<sup>6</sup> also found that the MH increased the ignition times. Increasing WF in the

**TABLE II**  
Fire Resistance Results of the WPC Panels

WPC panel formulation <sup>a</sup>	FR level		TSP <sup>b</sup>	PHRR <sup>b</sup>	tPHRR <sup>b</sup>	AHRR-60 <sup>b</sup>	AHRR-180 <sup>b</sup>	AHRR-300 <sup>b</sup>	AEHOC <sup>b</sup>	AMLR10-90 <sup>b</sup>	ASEA <sup>b</sup>
	Vol (%)	Wt (%)									
WF-40	0	0	18.8 F (1.1)	505 A (19)	62 A (5)	440 A (14)	392 A (16)	361 A (22)	32.6 A (0.4)	10.0 A (0.4)	454 A (88)
WF-50	0	0	23.8 DE (1.0)	401 B (14)	55 ABC (9)	346 B (4)	294 B (3)	266 B (4)	29.7 B (0.7)	9.1 BC (0.3)	458 A (22)
WF-60	0	0	23.7 DE (2.0)	362 C (5)	44 DE (2)	300 C (3)	249 C (2)	220 C (3)	25.9 CD (0.4)	9.2 BC (0.4)	381 AB (72)
WF-70	0	0	22.0 E (0.6)	325 DE (16)	44 DE (0)	268 D (6)	221 D (5)	197 D (6)	22.8 E (0.6)	9.7 AB (0.2)	326 AB (15)
WF-ZB	1.4	5	24.2 CDE (0.5)	351 CD (8)	47 CDE (2)	289 C (5)	249 C (3)	224 C (4)	28.0 BC (0.3)	8.0 D (0.1)	377 AB (84)
WF-MH	1.7	5	28.2 AB (0.4)	359 CD (12)	51 BCD (3)	295 C (7)	254 C (7)	230 C (8)	27.6 BC (0.6)	8.9 C (0.2)	312 AB (51)
WF-APP	2.1	5	25.7 BCD (0.6)	346 CD (32)	40 E (2)	252 DE (12)	196 E (11)	174 E (9)	26.1 CD (2.0)	6.8 E (0.3)	473 A (94)
WF-ZB	4.3	15	27.2 ABC (1.9)	303 EF (1.6)	53 ABCD (5.5)	246 E (6)	200 E (2)	177 DE (2)	25.2 D (0.7)	7.0 E (0.1)	339 AB (70)
WF-MH	5.0	15	30.4 A (2.3)	295 EF (8)	59 AB (1)	240 E (6)	194 E (8)	171 E (7)	25.3 D (1.0)	7.1 E (0.1)	260 B <sup>c</sup> (51)
WF-APP	6.3	15	27.8 AB (1.5)	277 F (8)	43 DE (2)	212 F (6)	161 F (2)	141 F (2)	22.5 E (1.0)	6.5 E (0.5)	490 A (99)

<sup>a</sup> See Table 1 for composition of samples. ZB, zinc borate; MH, magnesium hydroxide; APP, ammonium polyphosphate.

<sup>b</sup> Groups with same letters in column indicate that there is no statistical difference ( $p < 0.01$ ) in the means between the WPC panels according to Duncan's multiple range test. Values in parentheses are standard deviations. TSP, times for sustained ignition; PHRR, initial peak heat release rate; tPHRR, time of initial peak heat release rate; AHRR-60, average heat release rate over 60 s after observation of sustained ignition; AHRR-180, average heat release rate over 180 s after observation of sustained ignition; AHRR-300, average heat release rate over 300 s after observation of sustained ignition; AEHOC, average effective heat of combustion; AMLR 10–90, average mass loss rate for 10–90% of ultimate mass loss; ASEA, average smoke extinction area.

<sup>c</sup> Value calculated for two replicates. One outlier deleted. Mean was 177 and standard deviation 150 with outlier included.

untreated specimens by 10 and 20 wt % (WF-60 and WF-70) did not affect the ignition times (Table II). The times for the initial peak heat release rate (tPHRR, s) were also recorded (Table II). Of the treated specimens, the MH treatment had the longest tPHRR for given treatment level (59 s for 15 wt % treatment and 51 s for 5 wt % treatment) but tPHRR for 40 wt % WF (WF-40) and 50 wt % WF (WF-50) were 62 s and 55 s, respectively. The statistical significance of the differences ( $P < 0.01$ ) based on the Duncan's multiply range test is noted in Table II.

All three FR treatments reduced the heat release rate compared with the 50 wt % WF (WF-50) untreated specimens (Table II). Of the three treatments, the APP treatment had the most impact on the heat release rates as shown by the results for the PHRR and the various averages (AHRR-60, -180, -300; Table II). For the average heat release rates, the mean for the 5 wt % APP treatment was equivalent to the means for the 15 wt % ZB and 15 wt % MH treatments (Table II and Fig. 1). The differences between the APP treatment and the MH or ZB treatments were most obvious in the 300 s averages and the 5 wt % treatment levels. For the APP treatment, the marginal improvement in AHRR-300 for increasing the treatment level from 5 to 15 wt % was less than that for the MH and ZB treatments. For the 60, 180, and 300 s averages, the differences in the mean for the 15 wt % APP from the means for the other treatments and the untreated specimens were statistically significant based on the Duncan's multiply range test is noted in Table II. In similar studies, Stark et al.<sup>6</sup> and Ayrilmis et al.<sup>12</sup> also found that treatment with APP resulted in the most reductions in the average heat release rates. For PHRR, the means for the three treatments were not significantly different for a given treatment level (5 and 15 wt %) but the PHRR for the 5 and 15 wt % treatment levels were significantly different.

The APP treatment was also most effective in reducing the AEHOC and AMLR10-90 compared with the MH and ZB treatments. The differences in mean AEHOC for given treatment were statistically significant for the 15 wt % treatment level but not for the 5 wt % treatment level (Table II). In an initial study using a treatment level of 10 wt %, a dicabromodiphenyl oxide treatment was found to lower the AEHOC more than APP.<sup>12</sup> In contrast, the differences in mean AMLR10-90 for given treatment were statistically significant for the 5% treatment level but not for the 15 wt % treatment level. With the APP treatment, the marginal improvement in AMLR10-90 and AEHOC for increasing treatment level from 5 to 15 wt % was less than the improvement gained by the 5 wt % treatment over the 50% WF specimens. The improvements were linear for the MH and ZB treatments.

The lowest mean value for specific extinction area (ASEA) was obtained for the 15 wt % MH treatment but the mean was not statistically different than most of the other results (Table II). This conclusion was the same regardless whether the mean for WF-MH 15 wt % was 260 with an outlier removed (Table II) or 177 with it included. Due to the considerable variability in the ASEA data, the means for the different types of specimens were not statistically different (Table II). In an initial study using a treatment level of 10 wt %, a dicabromodiphenyl oxide treatment had significantly higher ASEA than the other treatments reported.<sup>12</sup>

Although all WPC panels had a constant density of about 800 kg/m<sup>3</sup>, the porosity contents of the WPCs containing FR were higher than those of the WPCs without FR at 50 wt % of the WF. As shown in Table I, the porosity contents of the WPC panels increased with increasing volume percentage of the FRs. This was mainly attributed to different densities of the FRs. For example, at the same WF content by volume, the porosity contents of the WPC panels without FR (50 wt % WF) and with 15 wt % ZB were 25.2% and 34.1%, respectively. Higher PP content in the WF-50 formulation resulted in a decrease in the porosity of the WPC, as it melts around 210°C in the hot press. However, the inorganic particles of the FRs used in the experiments do not melt in the WPC during hot pressing because of their higher melting temperatures. For this reason, they stay as powder in the WPC and increase the porosity content of the WPCs. Based on the findings obtained from the fire tests, it can be said that the AMLR HRR, AEHOC, and ASEA decreased with increasing porosity (decreasing volume %) of the WPCs without FR since polymer content decreased. A similar trend was also observed for the WPCs containing FR. Volume percentages of the WPCs containing FRs decreased when the FR content increased from 5 to 15 wt %. This resulted in an increase in the fire resistance of the WPCs. However, this trend was not observed for the WPCs at the same FR content by weight. For example, the WPCs containing APP showed better fire resistance as compared to the ZB and MH treatments although the APP treatment's porosity was lower than others (Table I). Since density of the APP is lower among the FRs, its volume percentage in the WPC is higher than others at the same FR content, by weight (Table I). Phosphorous compounds generally increase the amount of carbonaceous residue or char formed. APP is very efficient halogen free flame retardant mainly used in polyolefins.

When heated, APP decompose to form ammonia and phosphoric acid that in turn chars the material and shields it from releasing of flammable gases feeding flames. The phosphoric acid reacts with

alcohol groups to form heat-unstable phosphate esters. The esters decompose to release carbon dioxide and regenerate the phosphoric acid catalyst. The release of inflammable carbon dioxide while burning could lead to dilution of combustible fuel, reduction in oxygen concentration and hence reduction in burning rates. The resultant carbonaceous char is less-flammable than before. APP also lowers smoke production and helps resist flame migration.<sup>6</sup>

### Water resistance

Table III shows TS and WA values of the WPC panel formulations depending FR type and loading levels. Letters in Table III, show significant differences ( $P < 0.01$ ). The water resistance of the WPC panels was negatively affected by increasing FR content. For example, the average TS and WA values of the WF-ZB formulation at 5 wt % ZB after 112 days of submersion was 6.54 and 42.78% as compared to 15 wt % ZB, which were 7.12% and 47.76%. At the same WF content (50 wt % WF), the lowest TS and WA values were obtained from the WPC panels without FR, and then followed by the panels containing ZB, MH, and APP at 5 and 15 wt % WF levels. The TS and WA values of the panels containing 15 wt % APP were after 112 days of submersion 8.32 and 51.40% while they were found as 6.35 and 41.12% for the panels without FR at 50 wt % WF content, respectively. Similar results were also observed by Ayrylmis et al.<sup>12</sup> They reported that WPC panels containing ZB had the lowest TS and WA values while the highest values was found for the APP formulation.

Wood-based panel standards were used here for comparison of the TS and the WA values since there was no established maximum property for the WPC. One-day TS values of all WPC formulations met particleboard Type 7 (9%) and MDF Type HLS (10%) maximum requirements (1-day) for heavy-duty load-bearing boards for use in humid conditions of EN 312<sup>20</sup> and EN 622-5,<sup>21</sup> respectively. The TS and WA values of the WPC panels containing FRs were also less than those of wood-based panels such as MDF and oriented strandboard (OSB) containing FRs because the matrix polymers are hydrophobic. In a previous study, it was reported that TS values of the OSB and MDF panels containing FR, 6% borax based on the oven dried weight of wood, were found as 18.82 and 16.18%, respectively.<sup>3</sup>

Most intumescent FRs have some problems such as moisture sensitivity and poor compatibility with polymer matrix. For example, APP, a well known component of the intumescent FR systems is easily attacked by moisture (or water), migrates to the surface, and leads to a decrease in the properties.<sup>22</sup> The water resistance of the WPC panels without FR was

TABLE III  
Physical Properties of the WPC Panels

WPC panel formulation <sup>a</sup> (%)	vol Wt (%)	Thickness swelling (TS) <sup>b</sup>						Water absorption (WA) <sup>b</sup>					
		1 Day	7 days	28 Days	56 Days	112 days	1 Day	7 Days	28 days	56 days	112 days		
WF-40	0	1.21 A (0.31)	2.99 A (0.57)	3.95 A (0.36)	4.12 A (0.45)	4.54 A (0.45)	3.27 A (0.40)	13.34 A (1.46)	19.10 A (2.22)	23.56 A (2.71)	26.32 A (2.86)		
WF-50	0	1.67 B (0.23)	4.86 B (0.37)	5.85 B (0.35)	6.11 B (0.92)	6.35 B (0.93)	5.92 B (0.49)	19.51 B (1.49)	29.59 B (4.76)	34.43 B (4.21)	41.12 B (4.23)		
WF-60	0	3.19 C (0.39)	7.03 C (0.62)	8.36 CG (0.67)	8.47 CH (0.77)	8.67 CH (0.72)	8.52 C (0.81)	26.14 C (1.94)	44.27 C (4.92)	47.45 C (4.12)	54.12 C (4.56)		
WF-70	0	4.89 D (0.43)	9.77 D (0.71)	10.47 D (0.69)	10.94 D (0.82)	11.34 D (0.76)	11.77 D (0.93)	32.96 D (1.85)	52.9 D (4.78)	54.32 D (4.73)	57.83 D (5.28)		
WF-ZB	1.4	1.72 B (0.22)	4.95 B (0.43)	5.92 B (0.37)	6.19 BF (0.26)	6.54 B (0.40)	6.12 B (0.37)	20.15 BE (0.98)	31.07 BE (1.75)	35.82 BE (2.32)	42.78 BE (4.53)		
WF-MH	1.7	2.10 EF (0.31)	5.25 E (0.41)	6.25 BEF (0.41)	6.58 BF (0.37)	7.15 EF (0.53)	6.98 DE (0.29)	21.76 F (1.32)	34.26 F (1.87)	38.92 EF (3.35)	45.65 EF (4.12)		
WF-APP	2.1	2.35 FG (0.41)	5.74 E (0.46)	6.67 EF (0.60)	7.34 E (0.54)	7.75 FG (0.47)	7.33 EF (0.35)	23.32 G (1.26)	36.55 G (2.13)	40.33 F (3.29)	46.38 FG (4.32)		
WF-ZB	4.3	1.52 B (0.37)	5.49 E (0.34)	6.13 B (0.53)	6.64 F (0.35)	7.12 EFG (0.51)	7.45 EF (0.43)	24.23 GH (1.65)	38.19 H (2.30)	43.21 G (3.17)	47.76 GH (4.19)		
WF-MH	5.0	2.95 H (0.22)	6.65 FG (0.47)	7.46 G (0.54)	7.89 EG (0.64)	8.07 GH (0.62)	7.92 CF (0.51)	25.25 CH (1.78)	40.86 I (2.63)	44.82 GH (3.54)	50.17 I (5.27)		
WF-APP	6.3	3.07 C (0.30)	6.88 C (0.53)	7.94 G (0.63)	8.11 GH (0.51)	8.32 H (0.46)	8.15 C (0.67)	25.64 CH (1.97)	42.18 IJ (2.55)	45.57 GH (3.95)	51.40 I (4.97)		

<sup>a</sup> See Table 1 for composition of samples. ZB, zinc borate; MH, magnesium hydroxide; APP, ammonium polyphosphate.

<sup>b</sup> Groups with same letters in column indicate that there is no statistical difference ( $P < 0.01$ ) in the means between the WPC panels according Duncan's multiply range test. Values in parentheses are standard deviations.

**TABLE IV**  
**Mechanical Properties of the WPC Panels**

WPC panel formulation <sup>a</sup>	FR level		Modulus of rupture (MOR) <sup>b</sup> (N/mm <sup>2</sup> )	Modulus of elasticity (MOE) <sup>b</sup> (N/mm <sup>2</sup> )	Internal bond (IB) <sup>b</sup> (N/mm <sup>2</sup> )
	vol (%)	wt (%)			
WF-40	0	0	17.5 AF (0.54)	1816 A (149)	2.58 A (0.20)
WF-50	0	0	21.8 B (1.27)	2033 BFG (126)	1.92 B (0.18)
WF-60	0	0	18.3 AE (1.12)	2438 C (155)	1.65 C (0.16)
WF-70	0	0	15.1 CD (0.48)	2115 BE (134)	1.36 D (0.12)
WF-ZB	1.4	5	19.6 D (1.15)	2286 D (134)	1.88 BE (0.19)
WF-MH	1.7	5	18.0 E (0.93)	2102 EF (135)	1.79 E (0.15)
WF-APP	2.1	5	17.6 AF (1.10)	2055 BFG (104)	1.76 E (0.14)
WF-ZB	4.3	15	17.0 F (0.76)	2207 D (130)	1.60 CG (0.18)
WF-MH	5.0	15	15.1 CD (0.57)	2044 BFG (121)	1.54 CG (0.11)
WF-APP	6.3	15	14.7 D (0.61)	1996 G (105)	1.51 G (0.09)

<sup>a</sup> See Table 1 for composition of samples. ZB, zinc borate; MH, magnesium hydroxide; APP, ammonium polyphosphate.

<sup>b</sup> Groups with same letters in column indicate that there is no statistical difference ( $P < 0.01$ ) in the means between the WPC panels according Duncan's multiply range test. Values in parentheses are standard deviations.

better than the WPC panels containing FRs since the polymer content of the panels without FR was higher than that of the WPC panels containing FRs. For example, polymer content of WF-50 formulation was 48 wt % while it was 33 wt % for the WF-ZB formulation at 15 wt % FR level (Table I). This was mainly attributed to the hydrophobic character of the PP because of its being devoid of functional polar groups such as hydroxyls in the molecular and thus chemically inactive. The PP can crystallize on the WF and thereby wrapping WF better and leaving less exposed the wood on the WPC surface. With increasing FR content in the WPC at the same WF content (by weight), the TS and WA tend to increase as a larger share of the particle surface (WF and FR powder) is insufficiently bonded and protected by the plastic component. The greater connectivity between particles allows for easier moisture intrusion as compared to the WPC panels without FRs.

The base plastic material of WPC, such as neat PP, practically does not absorb water. Water absorption of WPCs depends on their porosity, amount of cellulose fiber, and their availability for incoming water. Because wood fiber or flour in WPC is exposed into pores, it also increases WA and TS of WPC. Wood extractives' decomposition produces VOC (volatile organic compounds), hence, porosity. In addition, plastic undergoes rather noticeable degradation, depolymerization, which leads to VOC formation. Along with it, moisture in cellulose fiber is converted to steam at hot melt temperatures and adds to microbubbling in the hot melt. When the material is immersed, water fills this void volume. This was agreement with previous studies in wood-based panels.<sup>23–25</sup> Vernois<sup>25</sup> reported that WA of wood increased with increasing porosity and when dipped in water it could absorb more than 20% of water.

The WA values of the WPC samples without FR increased with increasing porosity content. A similar trend was also observed for the WPCs containing FRs when the FR content increased from 5 to 15 wt % in the WPC. However, this trend was not observed for the WPCs at the same FR content by weight. As shown in Table I, the volume percentages of the FRs increased with decreasing density of the FR. For example, the APP had the highest volume percentage among the FRs due to its lower density. This resulted in higher WA and TS because increment of the volume percentage of the FR increased amount of the contaminated surface of the WF in the WPC. As known, the compatibility between WF and MAPP is negatively affected by the contaminated surface due to decreasing functional groups on the WF and MAPP.

FRs are hygroscopic in nature and they increase WA and TS values of wood and wood-based composites.<sup>26–28</sup> For example, due to their high affinity for water, phosphate-based FRs are hygroscopic FR chemicals used in the composite materials.<sup>27</sup> Ayrimis<sup>26</sup> found that TS and WA values of wood-based panels treated with phosphate based FRs such as MAP and DAP were higher than those of wood-based panels treated with borax and boric acid. Higher WA and TS values of the WPC panels containing APP was also attributed to its higher affinity for water as compared to the MH and ZB.<sup>12</sup>

### Mechanical properties

The IB values of the WPC panels were significantly affected by increasing content of the FRs (Table IV). The WPC panels without FR had higher IB strength than those of the WPC panels containing FRs at both loading levels. For example, The IB values of the

WPC panels containing 5 or 15 wt % ZB were  $1.88\text{N}/\text{mm}^2$  and  $1.60\text{N}/\text{mm}^2$ , respectively, while it was found as  $1.92\text{N}/\text{mm}^2$  for the WPC panels without FR at 50 wt % WF content. It was estimated that interfacial bonding between functional polar groups of the WF and MAPP was decreased by increasing volume percentage of the FR powder. The contamination of the wood surface resulted in poor compatibility between the WF and polymer matrix since some of the material stays as a powder on the outer surface of the WF. Deterioration of the mechanical properties of the filled and unfilled plastics with addition of FRs has been reported by some researchers.<sup>29,30</sup> A similar result was also found for MDF panels made from wood fibers treated with boron and phosphate compounds.<sup>31</sup>

The WF-ZB formulation had the highest IB value and then followed by the panels containing MH and APP at both loading levels. This is in agreement with a previous study by Ayrimlis et al.<sup>12</sup> They reported that WPC panels containing 10 wt % ZB had the highest IB value with  $1.81\text{N}/\text{mm}^2$  while the lowest one with  $1.58\text{N}/\text{mm}^2$  was found for the APP formulation. The IB values of all WPC formulations met particleboard Type 7 ( $0.75\text{N}/\text{mm}^2$ ) and MDF Type HLS ( $0.80\text{N}/\text{mm}^2$ ) minimum requirements of EN 312<sup>20</sup> and EN 622-5,<sup>21</sup> respectively. In addition, the IB values of the WPC formulations with FR were much higher than those of the wood-based panels containing FRs. In a previous study, it was reported that IB values of MDF and OSB panels containing 6% borax based on the oven dried weight of wood were found as  $0.68$  and  $0.49\text{N}/\text{mm}^2$ , respectively.<sup>3</sup>

The IB values of the WPCs decreased with increasing volume percentage of the WF since polymer content decreased in the WPC. This was mainly attributed to the decrease of the amount of binding between plastic and WF, since the WF content increased and so the amount of plastic decreased. Increment of the volume percentage of the FRs resulted in a decrease in the IB values of the WPCs. As mentioned before, due to its lower density, the APP had the highest volume percentage among the FRs. This resulted in higher contamination of the wood surface by the crystalline deposits of the APP and decreased interfacial bonding between WF and MAPP. Consequently, increasing volume percentage of the FR leads to weak interface between WF and coupling agent (MAPP) and poor overall mechanical properties. For this reason, the IB values of the WPC panels containing APP were lower than those of the WPC panels containing ZB and MH.

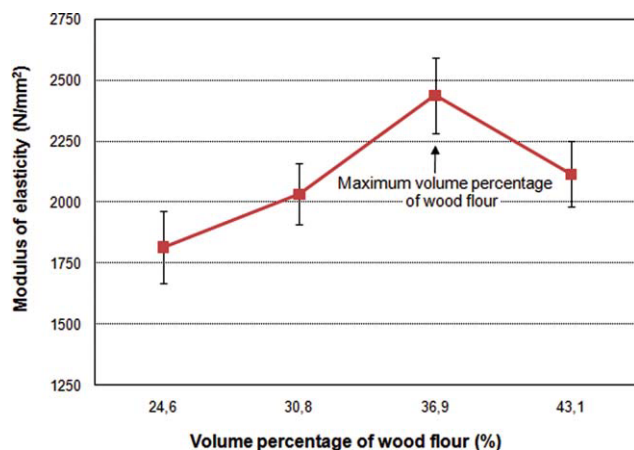
The flexural properties of the WPC panels with and without FR showed a similar trend to the IB results. The WPC panels containing FRs showed significant reductions in the MOR as compared to the WPC panels without FR at the same WF content (50

wt %), which were in agreement with literature.<sup>7,9,12</sup> For example, the average MOR value of the WF-ZB formulation containing 15 wt % ZB was  $17.0\text{N}/\text{mm}^2$  while it was found as  $21.8\text{N}/\text{mm}^2$  for the WPC-50 formulation without FR (Table IV). This could be attributed to the poor compatibility of the added FRs with the polymer. However, at the same WF content (50 wt %), the MOE values of the WPC samples containing FR, except for the 15 wt % APP treatment, were higher than those of the WPCs without FR due to lower polymer content. Letters in Table IV shows significant differences ( $P < 0.01$ ) between the average values of the WPC panel types. The WPC panels containing the ZB had the highest MOR and MOE values while the lowest values were found for the panels containing the APP in both 5 and 15 wt % levels of the FR. The MOR and MOE of the WPC panels were negatively affected by increasing volume percentages of the FRs. For example, the average MOR and MOE values of the WF-APP formulation at 2.1 vol % APP were  $17.6$  and  $2055\text{N}/\text{mm}^2$  as compared to 6.3 vol % APP which were  $14.7$  and  $1996\text{N}/\text{mm}^2$ . The MOR and MOE of all WPCs containing FR met particleboard minimum requirement for interior fitments including furniture manufacture ( $13$  and  $1800\text{N}/\text{mm}^2$ ) stated in EN 312.<sup>20</sup>

The flexural properties significantly increased to a certain volume percentage of the WF in the WPC panel. Further increment of the volume percentage of the WF resulted in a decrease in the MOR and MOE values since the polymer content decreased in the WPC panel. The flexural modulus of PP is lower than that of wood since major portion of the wood is crystalline cellulose.<sup>32</sup> The aligned fibril structure of the cellulose along with strong hydrogen bond has high stiffness.<sup>33</sup> At low volume percentage of the WF, a drastic decrease in the MOE was observed. The MOE of the samples without FR significantly increased with increase in volume content of the WF from 24.6 to 36.9% and then decreased as the volume content reached to 43.1% (Fig. 2). This has been explained with dilution of the polymer matrix and introduction of flaws at the fiber ends where high stress concentrations occur, causing the bond between fiber and matrix to break.<sup>34</sup> At high volume percentage of the WF, the polymer matrix was sufficiently restrained and the stress was more evenly distributed. This results in the reinforcement effect outweighing the dilution effect.<sup>35</sup> As the volume percentage of the WF is increased to a higher level, the flexural properties gradually improved to give a strength higher than that of the matrix. At very high volume percentage of the WF, the MOE again decreased due to insufficient matrix material (Fig. 2).<sup>34,35</sup>

Acids in wood, especially when accelerated by acidic FR treatments, hydrolyze cellulose and hemicellulose chains. Cellulose is often thought to





**Figure 2** Modulus of elasticity of the WPCs without FR as a function of the volume percentage (%) of the WF. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

be primarily responsible for the strength of the wood fiber; therefore, reducing the length of the cellulose molecules (degree of polymerization) would cause a reduction in macro-strength properties.<sup>36</sup> APP is an inorganic salt of polyphosphoric acid and ammonia. Middleton et al.<sup>37</sup> stated that FR treatments containing phosphate had more of an effect on strength properties of wood than that of borate. In a previous study, Myers and Holmes<sup>38</sup> reported that fiberboards containing APP had lower mechanical properties as compared to fiberboards containing borax. The decreases in the flexural properties of the WPC panels containing APP were probably due to embrittlement of the wood fibers caused by crystal formation within the wood cell walls or crosslinking between cellulose or hemicellulose molecules.

## CONCLUSIONS

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

1. The WPC panels incorporated with ZB gave an overall best performance in both water resistance and mechanical properties values followed by the WPC panels containing MH and APP. Due to its lower density and higher volume percentage in the WPC, the APP had the highest impact on the water resistance and mechanical properties of the WPCs, followed by the MH and ZB treatments, respectively.
2. The lower water resistance and mechanical properties of the WPC panels containing FRs were attributed to the contamination of the WF surface by the presence of loosely adhering crystalline deposits of FRs. The interfacial bonding between functional polar groups of

the WF and MAPP was decreased by increasing volume percentages of the FRs. Water resistance and mechanical properties of the WPCs were negatively affected by increasing volume percentages of the FRs.

3. Water resistance and mechanical properties of all WPC formulations containing FR met general-purpose particleboard requirements of EN 312. The TS and WA values of the WPC panels containing FRs were less than those of traditional wood-based panels such as particleboard and MDF because the matrix polymer is hydrophobic.
4. Except for higher initial peak heat release rates, the heat release rates in the cone calorimeter for the WPC panels treated with 5 wt % APP were comparable to the panels treated with 15 wt % ZB or 15 wt % MH. For these three FR's, the best fire resistance as measured in the cone calorimeter was obtained with the 15 wt % APP treatment.

This work was carried out while N. Ayrimis was visiting Professor at the Department of Wood Science, Hamburg University.

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