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Effects of fire retardants on physical, mechanical, and fire properties of flat-pressed WPCs

Nadir Ayrilmis · Jan T. Benthien · Heiko Thoemen · Robert H. White

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Abstract Physical, mechanical, and fire properties of the flat-pressed wood plastic composites (WPCs) incorporated with various fire retardants (10% by weight) at different levels of wood flour (WF) content, 40, 50, or 60 wt%, were investigated. The WPC panels were made from dry-blended WF, polypropylene (PP), and fire retardant (FR) powders with maleic anhydride-grafted PP (2 wt%) formulations using a conventional flat-pressing process under laboratory conditions. Incorporation of the fire retardants into the WPC panels significantly decreased the internal bond strength compared to the WPC panels without FR at all levels of the WF content. The modulus of rupture of the WPC panels containing FRs decreased with the increase in the WF content from 40 to 60 wt%. The modulus of elasticity increased with the increase in the WF content from 40 to 50 wt% and then decreased as the WF content reached 60 wt%. The WPC panels incorporated with zinc borate gave an overall best performance in both physical and mechanical properties followed by the panels treated with decabromodiphenyl oxide, magnesium hydroxide, and ammonium polyphosphate. Higher levels of the WF content resulted in significantly improved fire resistance of the WPC panels with and without FR as measured in the cone calorimeter. Of the four fire retardants tested, ammonium polyphosphate showed the most improvement over untreated ones.

N. Ayrilmis (✉)
Department of Wood Mechanics and Technology, Forestry Faculty, Istanbul University, Bahcekoy, Sariyer, 34473 Istanbul, Turkey
e-mail: nadiray@istanbul.edu.tr

J.T. Benthien
Mechanical Wood Technology, Department of Wood Science, Hamburg University, Leuschnerstrasse 91, 21031 Hamburg, Germany

H. Thoemen
Department of Architecture, Wood and Civil Engineering, Bern University of Applied Science, Solothurnstrasse 102, 2500 Biel 6, Switzerland

R.H. White
United States Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, USA

Einfluss von Brandschutzmitteln auf die physikalischen, mechanischen und Brandeigenschaften flachgepresster Holz-Kunststoff-Verbundplatten (WPC)

Zusammenfassung Die physikalischen, mechanischen und Brandeigenschaften flachgepresster Holz-Kunststoff-Verbundplatten (WPC) wurden mit verschiedenen Brandschutzmitteln (10% Masseanteil) mit unterschiedlichen Holzmehlanteilen (WF: 40, 50 und 60% Masseanteil) untersucht. Die WPC-Platten wurden trocken gemischt aus Holzmehl, Polypropylen (PP) und Brandschutzmitteln (FR) mit Maleinsaureanhydrid gepfropftem PP (2% Masseanteil) mit einer herkömmlichen Formulierung im Flachpressverfahren unter Laborbedingungen hergestellt. Die Zugabe von Brandschutzmittel in die WPC-Platten verringerte deren Querzugfestigkeit unabhängig vom Holzmehlanteil deutlich.

Die Biegefestigkeit der WPC-Platten mit FR nahm mit zunehmendem Holzmehlanteil von 40 bis 60% Masseanteil ab. Der Elastizitätsmodul nahm mit der Erhöhung des Holzmehlanteils von 40 bis 50% Masseanteil zu und nahm bei einem Holzmehlanteil von 60% wieder ab. Die mit Zinkborat hergestellten WPC-Platten wiesen im Allgemeinen die besten physikalischen und mechanischen Eigenschaften auf, gefolgt von den Platten, in die Decabromdiphenyloxid, Magnesiumhydroxid und Ammoniumpolyphosphat eingebracht wurde.

Gemessen im Kegelkalorimeter führten höhere Holzmehlanteile zu einem deutlich verbesserten Verhalten im Brandfall gegenüber den WPC-Platten mit oder ohne FR. Von den vier geprüften Brandschutzmitteln ergab Ammoniumpolyphosphat die beste Verbesserung gegenüber den unbehandelten Proben.

1 Introduction

Wood plastic composites (WPCs) have made significant gains in popularity over the last decade. Advantages of using wood as reinforcing filler in plastics include low cost, high relative strength and stiffness, low density and the fact that it is a natural resource. The predominant technologies to produce WPCs are extrusion to obtain endless profiles and injection moulding leading to 3-dimensional forms, although commercially less important. Another possibility which has only little been explored is to produce WPCs on a flat-press (Benthien et al. 2009). The advantage of this technology is that only a relatively low-pressure level is required, compared to extrusion and injection moulding. The productivity of the pressing technology is much higher than that of extrusion and injection moulding.

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. Fire retardants (FRs) for plastics and WPCs are completely different from those of wood materials (Klyosov 2007). Wood is typically impregnated with solutions of FRs, commonly salts, such as monoammonium and diammonium phosphate, ammonium sulfate, zinc chloride, sodium tetraborate, boric acid, and guanylurea phosphate (Wang et al. 2004; Ayrilmis et al. 2007). 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. 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 behaviour. The fire property of WPCs is not well understood, and there is little information regarding the effectiveness of various FRs in the public domain (Sain et al. 2004; Qing-Wen et al. 2005).

The objective of this study was to determine the effects of various FRs on the physical, mechanical, and fire properties of the WPC panels made using dry-blend method at different levels of the WF content. Cone calorimeter test was used to characterize the fire resistance of the treated WPC panels, and the results were compared with the untreated WPC panels. The present work is part of a broader study on the WPC panels. A more general description of the flat-pressing technology for WPC, and of the most important parameters affecting panel properties was given by Benthien et al. (2009).

2 Materials and methods

2.1 Materials

Commercial softwood WF (Jeluxyl WEHO 500V) used to produce WPC was obtained from a manufacturer (Jelu-Werk) of the 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. Polypropylene (PP) powder (Moplen HP500V) (T_m = 163°C, p = 0.91 g/cm^3, MFU230°C/2.16 kg = 120 g/10 min) produced by Basell Polyolefine GmbH (LyondellBasell Industries) in Wesseling, Germany, was used as the polymeric material. Maleic anhydride-grafted PP (MAPP) (Scona TP PP 8112 FA) powder was supplied by Kometra Ltd., 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-suppy (e) low-cost. The chemicals used in the experiments were found to be safe even under the worst-case exposure assumptions (NAS 2002).

Four FR systems (powder) were investigated:

(1) Ammonium polyphosphate (APP) (Exolit AP 422, Clariant Corp., Frankfurt, Germany)
(2) Decabromodiphenyl oxide (BR) (Saytex 102E, Albemarle Corp., Neuve, Belgium)
(3) Magnesium hydroxide (MH) (Apymag 80S, Nabaltec AG, Schwandorf, Germany)
(4) Zinc borate (ZB) (Balmumcu Chemical Com., Istanbul, Turkey)

WPC panels incorporated with 10 wt% of the FR system had 40, 50, or 60 wt% application levels of the WF content. This allowed composites to be compared based on different levels of the WF content. Table 1 shows the raw material formulations used for the WPC panels.

2.2 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 powders, 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 mm × 450 mm forming frame. Wax paper was used to avoid direct contact of the PP powder with the

Table 1 Compositions of the WPC panel formulations at different levels (wt%) of wood flour content
Tab. 1 Rezeptur der WPC-Platten mit verschiedenen Holzmehlanteilen (WF)

WPC panel fomulation	FR chemical content (wt%)	Phase I			Phase II			Phase III		
		40 wt% WF loading level			50 wt% WF loading level			60 wt% WF loading level		
		PP(%)	WF(%)	MAPP(%)	PP(%)	WF(%)	MAPP(%)	PP(%)	WF(%)	MAPP(%)
WF	–	58	40	2	48	50	2	38	60	2
WF-ZB	10	48	40	2	38	50	2	28	60	2
WF-BR	10	48	40	2	38	50	2	28	60	2
WF-MH	10	48	40	2	38	50	2	28	60	2
WF-APP	10	48	40	2	38	50	2	28	60	2

PP: polypropylene, W F wood flour, MAPP: maleic anhydride-grafted PP, ZB: zinc borate, BR: decabromodiphenyl oxide, MH: magnesium hydroxide, APP: ammonium polyphosphate

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 N/cm^2, 210°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 conditioned for one-week in the climate room having 65% relative humidity (RH) and 20°C before they were cut into test specimens. Ten mm thick panels were then trimmed to a final size of 420 mm × 420 mm. A total of 45 experimental panels, three for each type of panel, were manufactured. The average density value of the panels was 800 kg/m^3.

2.3 Fire resistance

Heat release measurements were conducted in accordance with ASTM E 1354 (ASTM International 2008). Three replicate samples were tested for each type of specimen. Samples were 100 mm × 100 mm and sample thickness was 10 mm. 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 seconds criteria for sustained ignition for observing the time for sustained ignition of the specimen.

2.4 Determination of water resistance

The water resistance of the WPC specimens, thickness swelling (TS) and water absorption (WA), was evaluated according to EN 317 (1993). Eighteen replicate samples with dimensions of 50 mm × 50 mm × 10 mm were used for each type of WPC panel to determine the TS and WA. The specimens conditioned at 20°C and 65% RH were placed in a container of water maintained at a temperature of 20°C. The weights and thicknesses of the specimens 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 specimens were removed from the water, all surface water was wiped off with a dry cloth, and weighed to the nearest 0.001 g and measured to the nearest 0.01 mm immediately. The specimen thickness was determined by taking a measurement at a specific location, the diagonal cross-point, on the sample. Density of the specimens was evaluated according to the test method and requirement of EN 323 (1993).

2.5 Determination of mechanical properties

The flexural properties (modulus of rupture (MOR) and modulus of elasticity (MOE)) of the specimens conditioned at 20°C and 65% RH were conducted according to EN 310 (1993). Fifteen replicate samples with dimensions of 250 mm x 50 mm x 10 mm were used for each type of WPC panel to determine the flexural properties. The specimens 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. Load-deflection data for the calculation of the specimen's MOE were recorded at the 10 and 40% values of failure load (P_{max}). The crosshead speed was adjusted so that failure would occur within an average of 60 ± 10 s. The IB test was conducted on the specimens cut from the experimental WPC panels according to EN 3 19 (1993). Eighteen replicate samples with dimensions of 50 mm × 50 mm × 10 mm were used for each type of panel to determine the IB strength.

2.6 Statistical analysis

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

3 Results and discussion

3.1 Fire resistance

The primary result from the cone calorimeter test is a heat release rate (HRR) curve over the duration of the test (Figs. 1, 2, 3). In the cone calorimeter test, the HRR is the heat evolved from the specimen due to combustion and is determined by measuring the oxygen consumed during burning (ASTM International 2008). For reporting purposes (Table 2), the heat release curves were reduced to single numbers via the recorded initial peak HRR and calculated averages of the HRR over a set time (60 seconds, 180 seconds, and 300 seconds) after ignition of the specimen was observed. The total heat release (THR) is the cumulative heat release over the duration of the test. Other results include times for sustained ignition (TSI), the average mass loss rate (AMLR), average specific extinction area (ASEA) and average effective heat of combustion (AEHOC) for the test duration (Table 2). The AMLR was the average for the data from 10% to 90% of the ultimate mass loss. The ASEA is a measurement of the smoke obscuration as measured using a laser beam through the exhaust duct. The AEHOC is the measured heat release divided by the mass loss for the duration of the test.

Increasing the percentage WF (i.e. decreasing percentage polypropylene) in the untreated and treated specimens reduced the heat release as reflected in the results for the peak and average heat release rates, THR, and AEHOC (Table 2). For these results, the untreated specimens consistantly had higher heat release compared with the comparable treated specimens. The untreated 40 wt% WF, 58 wt% PP speci-

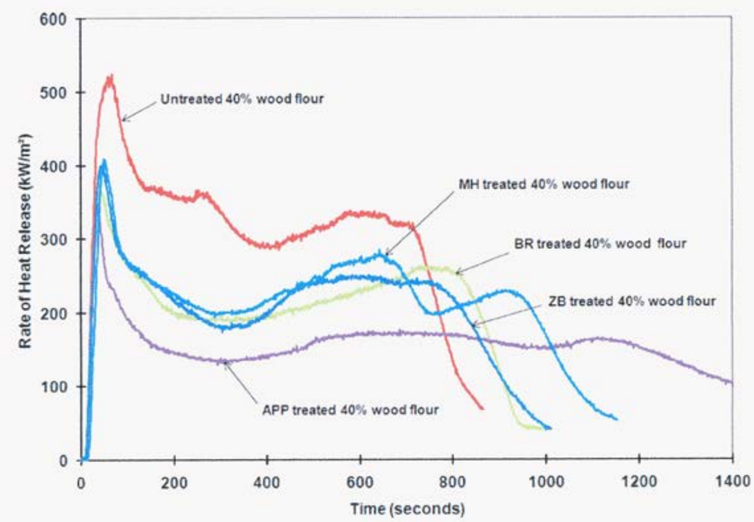

Fig. 1 Heat release curves of the untreated and treated WPC panels at 40 wt% wood flour level from cone calorimeter tests
Abb. 1 Wäremefreisetzungskurven der unbehandelten und behandelten WE-Platten mit 40% Masseanteil an WF im Kegelkalorimeterversuch

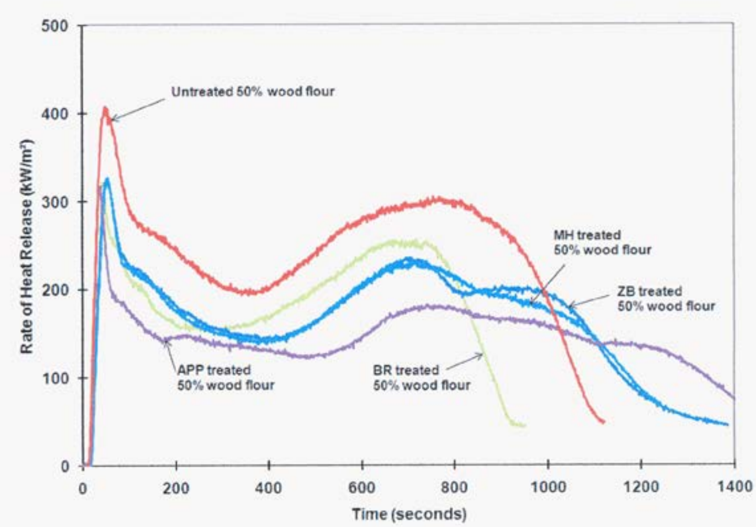

Fig. 2 Heat release curves of the untreated and treated WPC panels at 50 wt% wood flour level from cone calorimeter tests
Abb. 2 Wäremefreisetzungskurven der unbehandelten und behandelten WE-Platten mit 50% Masseanteil an WF im Kegelkalorimeterversuch

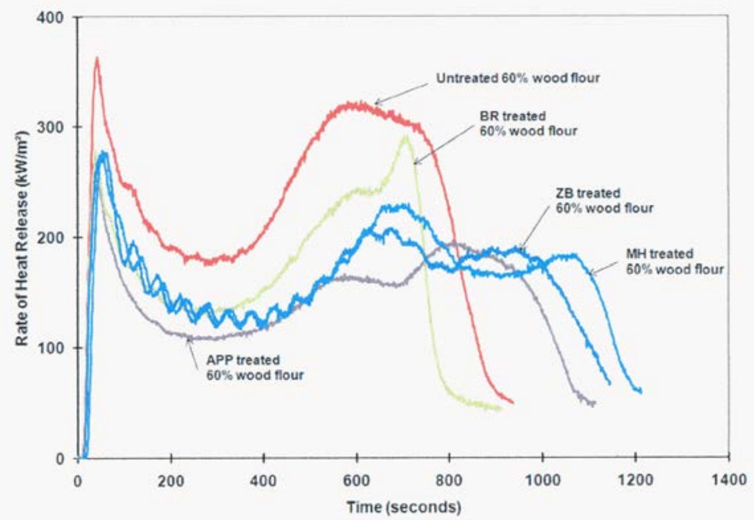

Fig. 3 Heat release curves of the untreated and treated WPC panels at 60 wt% wood flour level from cone calorimeter tests
Abb. 3 Wäremefreisetzungs-kurven der unbehandelten und behandelten WPC-Platten mit 60% Masseanteil an WF im Kegelkalorimeterversuch

mens had the highest peak and average HRR's, highest mean AEHOC, and highest mean THR (Table 2). Increasing the WF content of the untreated specimens to the 60 wt% level produced heat release rate curves comparable or less than those for the 40 wt% WF treated specimens except the APP treatment (Fig. 3). Increasing the WF content had minimal and conflicting effects on the AMLR. Increasing the percentage WF also generally reduced the ASEA but only increased some of the results for the TSI.

The ammonium polyphosphate (APP) treatment was the most effective treatment in reducing the peak and average HRR's from that of the untreated specimens (Table 2). The differences between the different treatments were generally not significant for the peak HRR. The reductions in the HRR from that of the untreated were greatest for the 40 wt% WF content specimens. The APP treated specimens also had the lowest AMLR for the 40 and 50 wt% WF levels. In terms of the TSI, THR and AEHOC, the APP treated specimens were more comparable with the other treated specimens. These results suggest that the reductions in heat release rate with the APP treatment is due to the combined effects of reduced mass loss rate and reduced effective heat of combustion. The ASEA results for the APP treated specimens were comparable to untreated specimens. In a similar study of five fire-retardant treatments of polyethylene WPCs, Stark et al. (2010) also found APP treatment to be most effective in reducing the HRR.

The magnesium hydroxide (MH) treatment was the most effective treatment in increasing the TSI from that of the untreated specimens, particularly for the 60 wt% WF specimens. The HRR results for the MH treated specimens were less than the untreated and Comparable to the BR and ZB treated specimens. The reductions in AEHOC from the untreated specimens for the MH treated specimens were less than APP and BR and comparable to ZB treated specimens. The reductions in AMLR from the untreated specimens for the MH treated specimens were less than the APP for 40 ana 50 wt% WF content specimens.

The decabromodiphenyl oxide (BR) treatment was the most effective treatment in decreasing the AEHOC from that of the untreated specimens. In contrast, the BR had AMLR that were comparable or higher than AMLR for the untreated specimens. The HRR results for the BR treated specimens were comparable to the ZB and MH treated specimens but the THR results were less. The ASEA results for the BR treated specimens were much higher than the untreated and the other treated specimens. These results suggest that the primarily mechanism affecting HRR results for the BR treatment was reductions in the effective heat of combustion including that due to the high smoke production.

The zinc borate (ZB) and MH treatments were the most effective treatments in decreasing the ASEA from that of the untreated specimens. The ZB is a known smoke suppressant (Weil 2000). The HRR results for the ZB treated specimens were comparable to the BR and MH treated specimens. The TSI results for the ZB treated specimens were comparable to the BR treated specimens and untreated specimens. The AEHOC and THR results for the ZB specimens were comparable to the MH treated specimens with the smallest reductions from results for the untreated specimens. AMLR results for the ZB specimens were also similar to the results for the MH treated specimens and less than that for the untreated specimens.

The exchange of the PP by the WF in the WPC panel leads to a significant reduction of the peak HHR and the other relevant cone parameters. As shown in Table 2, when the WF content increased from 40 to 60 wt% for the untreated samples, the peak HRR decreased by 28%. In general, at the same PP content, the fire resistance of the treated WPC panels was better than that of the untreated WPC panels. This was mainly attributed to the fire retardant mechanisms of the chemicals used in the experiments

Table 2 Fire properties of the WPC panels containing 10 wt% fire retardant at different levels of wood flour content

Tab. 2 Brandschutzeigenschaften der WPC-Platten mit 10% Masseanteil an Brandschutzmittel bei verschiedenen Holmehlanteilen (WF)

WPC panel	Level of WF	Heat release rate (kW/m²)				Other results				
formulation	content (wt%)	peak	60 s	180 s	300 s	TSI (s)	AEHOC (MJ/kg)	ASEA (m²/kg)	THR (MJ/m²)	AMLR (g/m²s)
WF-40	40	505 A[a] (19)	440 A (14)	392 A (16)	361 A (22)	18.8 D (1.1)	32.6 A (0.4)	545 CE (89)	253 AB (17)	10.0 B (0.4)
WF-ZB		402 B (3)	327 C (4)	275 CD (2)	246 CD (4)	21.5 C (2.6)	29.8 BC (1.2)	396 CE (84)	237 BD (25)	7.7 DE (0.1)
WF-BR		371 C (8)	313 CD (6)	262 D (2)	234 DE (1)	21.0 CD (0.3)	22.8 F (0.1)	913 A (101)	200 EH (9)	9.9 B (0.1)
WF-MH		407 B (3)	325 C (3)	277 C (3)	252 BC (6)	25.0 BC (1.3)	30.1 B (0.4)	446 CE (38)	249 AC (6)	8.0 D (0.1)
WF-APP		342 DE (15)	264 E (1)	200 G (4)	177 GH (4)	24.2 BC (3.2)	28.0 CD (1.7)	571 BC (32)	225 CE (6)	5.9 G (0.1)
WF-50	50	401 B (14)	346 B (4)	294 B (3)	266 B (4)	23.8 BC (1.0)	29.7 BC (0.7)	458 CE (22)	270 A (4)	9.1 c (0.2)
WF-ZB		337 DE (13)	273 E (4)	230 F (4)	201 F (5)	25.1 BC (2.8)	27.2 DE (0.5)	298 E (51)	216 DG (10)	7.4 E (0.4)
WF-BR		320 E (6)	264 E (6)	216 F (5)	193 FG (5)	24.7 BC (1.6)	20.3 G (0.6)	846 A (57)	182 H (5)	10.1 B (0.2)
WF-MH		330 E (6)	265 E (3)	223 F (3)	196 F (2)	27.6 AB (2.0)	26.3 DE (0.6)	348 DE (52)	212 DG (8)	7.4 DE (0.2)
WF-APP		316 E (9)	234 F (9)	181 H (5)	161 H (5)	24.6 BC (1.2)	24.1 F (0.1)	518 BD (134)	196 FH (10)	6.4 F (0.l)
WF-60	60	362 CD (5)	300 D (3)	249 E (2)	220 E (3)	23.7 BC (1.6)	25.9 E (0.4)	381 DE (72)	220 DF (8)	9.2 C (0.4)
WF-ZB		276 F (6)	238 F (8)	188 GH (4)	166 H (3)	23.5 BC (0.7)	23.2 F (0.8)	346 ED (33)	184 H (9)	7.4 E (0.2)
WF-BR		283 F (10)	235 F (6)	188 GH (8)	167 H (6)	24.4 BC (1.3)	17.4 H (0.1)	637 B (103)	156 I (7)	10.9 A (0.1)
WF-MH		277 F (9)	233 F (6)	186 H (4)	163 H (4)	29.2 A (0.8)	23.9 F (0.6)	293 E (52)	191 GH (7)	7.2 E (0.2)
WF-APP		279 F (17)	216 G (5)	160 I (5)	139 I (4)	23.2 C (0.8)	21.1 G (0.8)	419 CE (30)	151 I (8)	7.2 E (0.3)

[a]Groups with same letters in column indicate that there is no statistical difference ($p < 0.01$) between the specimens according to Duncan's multiple range test of the means. Values in parentheses are standard deviations for three replicates (WF-MH-40 had two replicates). WF: wood flour, ZB: zinc borate, BR: decabromodiphenyl oxide, MH: magnesium hydroxide, APP: ammonium polyphosphate. TSI: times to sustained ignition, THR: total heat released, AEHOC: average effective heat of combustion, AMLR average mass loss rate for 10% to 90% mass loss, ASEA: average specific extinction area

Table 3 Water resistance of the WPC panels containing 10 wt% fire retardant at different levels of wood flout content

Tab. 3 Feuchteverhalten der WPC-Platten mit 10% Masseanteil an Brandschutzmittel bei verschiedenen Holzmehlanteilen

WPC panel formulation	Level of WF content (wt%)	Thickness swelling					Water absorption				
		1 day (%)	7 days (%)	28 days (%)	56 days (%)	112 days (%)	1 day (%)	7 days (8)	28 days (%)	56 days (%)	112 days (8)
WF-40	40	1.21 A[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-ZB		1.35 AB (0.20)	3.39 AB (0.49)	4.38 AB (0.42)	4.54 AB (0.69)	4.96 AB (0.78)	3.72 AB (0.38)	14.33 AB (1.34)	22.84 B (2.36)	26.24 AB (2.34)	30.46 B (2.73)
WF-BR		1.42 ABC (0.24)	3.62 B (0.33)	4.79 BC (0.38)	5.05 BC (0.74)	5.23 B (0.45)	4.55 AC (0.47)	15.27 BC (1.39)	25.64 C (2.58)	28.78 BC (2.88)	32.54 BC (3.66)
WF-MH		1.51 BC (0.33)	4.29 C (0.59)	5.26 CD (0.44)	5.56 C (0.79)	5.98 C (0.62)	5.15 BCD (0.41)	16.58 C (1.56)	26.86 CD (2.52)	30.19 C (3.54)	35.88 CD (4.43)
WF-APP		1.59 C (0.27)	4.77 D (0.41)	5.62 DE (0.46)	5.84 CD (0.72)	6.24 CD (0.71)	5.58 CDE (0.53)	18.63 D (1.67)	27.69 CD (2.13)	31.40 CD (3.27)	37.16 CD (4.81)
WF-50	50	1.67 CD (0.23)	4.86 D (0.37)	5.85 E (0.35)	6.11 CD (0.92)	6.35 CD (0.93)	5.92 CDE (0.49)	19.51 D (1.49)	29.59 D (4.76)	34.43 DE (4.21)	41.12 DE (5.23)
WF-ZB		1.89 DE (0.37)	5.42 E (0.46)	6.08 E (0.47)	6.19 D (0.77)	6.52 D (0.70)	6.23 DEF (0.56)	21.77 E (1.60)	32.44 E (3.87)	36.98 EF (4.45)	43.14 EF (4.76)
WF-BR		2.10 E (0.30)	5.85 F (0.53)	6.88 F (0.41)	7.05 E (0.82)	7.21 E (0.83)	6.94 EG (0.49)	22.23 E (1.73)	35.18 EF (4.12)	39.54 FG (3.98)	45.49 EFG (4.23)
WF-MH		2.58 F (0.45)	6.35 G (0.42)	7.46 G (0.52)	7.68 F (0.61)	7.92 F (0.56)	7.56 FG (0.63)	24.85 F (1.83)	39.94 G (4.45)	41.67 G (4.56)	48.17 FG (5.11)
WF-APP		2.83 F (0.38)	6.86 H (0.59)	8.11 H (0.64)	8.26 G (1.02)	8.44 G (0.91)	8.20 GH (0.76)	25.54 F (2.13)	41.23 G (3.39)	42.78 G (4.82)	49.59 G (4.65)
WF-60	60	3.19 G (0.39)	7.03 HG (0.62)	8.36 H (0.67)	8.47 G (0.77)	8.67 GH (0.72)	8.52 GJ (0.81)	26.14 FG (1.94)	44.27 H (4.92)	47.45 H (4.12)	54.12 H (5.56)
WF-ZB		3.26 G (0.34)	7.34 G (0.50)	8.44 HG (0.61)	8.55 G (1.09)	8.82 GH (0.59)	8.92 HIG (0.70)	26.84 GH (2.43)	45.16 HE (4.18)	49.13 HG (4.67)	57.77 HI (5.23)
WF-BR		3.70 H (0.41)	7.85 I (0.66)	8.58 G (0.72)	8.65 G (0.91)	9.02 HI (0.77)	9.85 IJK (0.82)	28.06 HI (2.85)	46.43 HEF (3.76)	52.78 GI (4.33)	59.22 IJ (5.76)
WF-MH		4.23 I (0.47)	8.48 J (0.58)	9.22 I (0.68)	9.33 H (0.71)	9.35 I (0.68)	10.23 IJK (1.12)	29.54 IJ (2.54)	47.75 EF (4.23)	54.16 I (4.48)	62.38 J (5.82)
WF-APP		4.85 J (0.52)	9.11 K (0.75)	9.95 J (0.78)	10.16 I (1.41)	10.12 J (1.02)	10.98 K (0.94)	30.28 J (2.79)	49.13 F (3.93)	55.32 I (5.06)	63.92 K (6.46)

[a]Groups with same letters in column indicate that there is no statistical difference ($p < 0.01$) between the specimens according to Duncan's multiple range test. Values in parentheses are standard deviations. WF: wood flour, ZB: zinc borate, BR: decabromodiphenyloxide, MH magnesium hydroxide, APP ammonium polyphosphate

(Klyosov 2007). However, increasing WF content of the untreated specimens to the 60 wt% level produced heat release rate curves comparable or less than those for the 40 wt% WF treated specimens except the APP treatment (Figs. 1 and 3).

3.2 Water resistance

Table 3 shows TS and WA values of the WPC panels depending on the chemical type at different levels of the WF. Significant differences are shown by letters in Table 3. Although TS values of the treated and untreated WPC panels increased with increasing submersion time, noticeable increases in the TS values after 28-days of submersion were not observed. The lowest TS and WA values were obtained from the WPC panels without FR, and then followed by the WPC panels containing ZB, BR, MH, and APP at all levels of the WF content, respectively. Most intumescent fire retardants have some problems such as moisture sensitivity and poor compatibility with polymer matrix. For example, APP, a well known component of the intumescent fire retardant systems is easily attacked by moisture (or water), migrates to the surface, and leads to a decrease in the properties (Wu et al. 2008). 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 for (one-day) heavy-duty load-bearing boards for use in humid conditions of EN 312 (2003) and EN 622-5 (2006), respectively.

The water resistance of the untreated WPC panels was better than that of the treated WPC panels at the same level of WF content since polymer content of the untreated panels was 10% higher than that of the treated panels. For example, polymer content of the untreated WF-40 formulation was 58 wt% while it was 48 wt% for the WF-ZB formulation at 40 wt% WF level. (Table 3). Incorporation of the ZB into the WPC panel at 40 wt% WF level increased the WA by 30.46% and the TS by 4.96% after 112-days of submersion. Similar results were also observed for other WPC formulations at 50 and 60 wt% WF levels. This was mainly attributed to the hydrophobic character of the PP. As shown in Benthien et al. (2009), increasing WF content in flat-pressed WPC-panels increased the TS and WA values due to the hydrophilic property of WF. This effect was also found for the untreated and treated WPC panels here. The water resistance of the WPC panels improved with increasing polymer content. The PP can crystallize on the WF and thereby wrapping WF better and leaving the wood on the WPC surface less exposed.

3.3 Mechanical properties

Table 4 summarizes mechanical properties of all the WPC formulations. The IB values were significantly affected by increasing content of the WF in the panel. Significant differences are shown by letters in Table 4. The untreated WPC panels had higher IB strength than those of the treated panels at all levels of WF content. This was attributed to contamination of the wood surface by the presence of loosely adhering crystalline deposits of FRs and resulted in poor compatibility between the WF and polymer matrix. Some of the material stays as a powder on the outer surface of the

Table 4 Mechanical properties of the WPC panels containing 10 wt% fire retardant at different levels of wood flour content
Tab. 4 Mechanische Eigenschaften der WPC-Platten mit 10% Masseanteil an Brandschutzmittel bei verschiedenen Holzmehlanteilen

WPC panel formulation	Level of WF content (wt%)	Modulus of rupture (N/mm^2)	Modulus of elasticity (N/mm^2)	Internal bond (N/mm^2)
WF-40	40	17.5 A[a] (0.54)	1816 A (149)	2.58 A (0.20)
WF-ZB		20.6 B (1.53)	2271 BC (131)	2.35 B (0.23)
WF-BR		19.8 BC (1.59)	2126 DE (110)	2.25 BC (0.31)
WF-MH		19.0 DC (1.27)	2085 DEG (119)	2.15 CD (0.19)
WF-APP		18.4 AD (2.18)	2014 FG (82)	2.07 D (0.27)
WF-50		21.8 E (1.27)	2033 DF (126)	1.92 E (0.18)
WF-ZB		17.5 A (0.63)	2317 C (119)	1.81 EF (0.17)
WF-BR		16.1 F (0.56)	2251 BC (121)	1.79 EFL (0.33)
WF-MH		15.5 FG (1.39)	2175 BE (118)	1.70 FG (0.15)
WF-APP		15.1 GH (1.25)	2126 DE (146)	1.58 GH (0.31)
WF-60	60	18.3 AD (1.12)	2438 H (155)	1.65 GL (0.16)
WF-ZB		14.5 H (1.37)	2083 DGE (99)	1.49 HI (0.14)
WF-BR		13.3 I (1.24)	1949 F (127)	1.38 IJ (0.17)
WF-MH		11.8 J (0.78)	1840 A (124)	1.31 J (0.13)
WF-APP		10.5 K (0.66)	1773 A (99)	1.25 J (0.11)

[a] Groups with same letters in column indicate that there is no statistical difference ($p < 0.01$) between the specimens according to Duncan's multiply range test. Values in parentheses are standard deviations. WF: wood flour, ZB: zinc borate, BR decabromodiphenyloxide, MH magnesium hydroxide, APP: ammonium polyphosphate

WF, thereby increasing the surface area of the solids within the mat and reducing the bonding efficiency of the polymer. A similar result was also found for MDF panels made from wood fibers treated with various FRs (Ayrilmis 2006).

With increasing WF content, the IB values of all the panel formulations decreased. This fact is due to decreasing the amount of binding between plastics and WF, since the WF content increases and thus the amount of plastic, as the adhesive, decreases. The WF-ZB formulation had the highest IB value while the lowest one was found for the WF-APP formulation at all levels of WF content. The IB values of all the WPC formulations met particleboard Type 7 (0.75 N/mm^2) and MDF Type HLS (0.80 N/mm^2) minimum requirements of EN 312 and EN 622-5, respectively.

The MOR of the WPC panels containing 10 wt% FR decreased with the increase in the WF content from 40 to 60 wt%. For example, the average MOR value of the WF-ZB formulation at 40 wt% WF level was 20.6 N/mm^2 as compared to 60 wt% WF level which was 14.5 N/mm^2. However, the MOE of the WPC panels containing 10 wt% FR increased with the increase in the WF content from 40 to 50 wt% and then decreased as the WF content reached 60 wt% (Table 4). This could be attributed to the poor compatibility of the added FRs with the polymer. It was estimated that interfacial bonding between the WF and PP was decreased by the FR powder. Deterioration of the mechanical properties of the filled and unfilled plastics with the addition of FRs has been reported by some researchers (Horn 2000; Chiu and Wang 1998). The results of the MOR and MOE tests were also in agreement with literature (Li and He 2004; Sain et al. 2004; Qing-Wen et al. 2005). The WPC panels containing ZB had the highest MOR and MOE values while the lowest values were found for the panels containing APP. The aspect of an optimal filler content, depending on the individual raw material formulation, was also shown for flat-pressed panels by Benthien et al. (2009).

4 Conclusions

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

(1) In the investigated FRs, the WPC panels incorporated with ZB gave an overall best performance in both the physical and mechanical properties followed by the WPC panels incorporated with BR, MH, and APP. The lowest TS and WA values were obtained from the WPC panels without FR, and then followed by the WPC panels with ZB, BR, MH, and APP at all levels of WF content.

(2) Adding 10 wt% FR into the WPC panel decreased the IB strength compared to the untreated WPC panels at all levels of WF content. The MOR of the treated WPC panels decreased with the increase in WF content from 40 to 60 wt%. The MOE of the treated WPC panels increased with the increase in WF content from 40 to 50 wt% and then decreased as the WF content reached 60 wt%.

(3) The APP treatment was the most effective treatment in reducing the peak and average HRR's from that of the untreated specimens.

(4) Higher levels of WF content resulted in significantly improved fire resistance of the WPC panels with and without FR as measured in the cone calorimeter test. Increasing the WF content of the untreated specimens to the 60 wt% level produced heat release rate curves comparable or less than those for the 40 wt% WF treated specimens except the APP treatment.

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