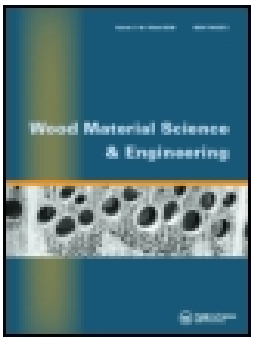

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ORIGINAL ARTICLE

Technological properties and fire performance of medium density fibreboard (MDF) treated with selected polyphosphate-based fire retardants

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ABSTRACT
The objective of the work was to evaluate the efficacy of two new polyphosphate-based fire retardants (FRs) and one commercial product named Siriono® on the fire performance and physical–mechanical properties of medium density fibreboard (MDF) fabricated in the laboratory from Scots pine (*Pinus sylvestris* L.) wood. The fibres were treated with aqueous solutions of fire retardants, at 12% loading (dry salt on dry wood), and bonded with a melamine urea formaldehyde (MUF) adhesive. The physical and mechanical properties of panels were assessed using the European standards, whereas their fire performance was evaluated using an in-house method and the Cone calorimeter. In overall, the chemicals added enhanced the fire and smoke properties of the panels to varying degrees. Critical FR parameters such as peak heat release rate (peak HRR), total heat release (THR) and total smoke production (TSP) were significantly improved in the FR-treated panels, as exhibited in cone calorimeter tests. However, the internal bond strength of treated panels largely decreased by the addition of fire retardants, while thickness swell and water absorption negatively affected to a significant extent. In contrast, the formaldehyde release of the panels was considerably decreased at the E1 class level, with the incorporation of the polyphosphate-based additives.

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KEYWORDS
Medium density fibreboard (MDF); fire performance; polyphosphate-based retardants; smoke suppressants

Introduction

Wood as an organic material is comprised of carbon, hydrogen and oxygen, and thus, is combustible. Wood and wood-based products should therefore be treated with fire retarding compounds, widely known as fire retardants (FRs). This is true both in building and construction to improve the fire performance, because strict fire safety standards have been imposed throughout Europe, in the recent years. In wood-based panels, several chemical compounds are used by the industry mostly in particleboard, oriented strand board (OSB) and medium density fibreboard (MDF), either in dry or liquid form (LeVan and Winandy 1990, White and Sweet 1992, Dunky 2003, Ayrilmiş 2007, Winandy *et al*. 2008, Abood *et al*. 2012, Mantanis *et al*. 2018, Esmailpour *et al.* in press).

Typically, fire retarded wood panels are prepared by treatments with phosphorus-, nitrogen-, zinc-, boron- and/or aluminium-containing compounds such as zinc borate ($2ZnO·3B_2O_3$), ammonium polyphosphate $(NH_4PO_3)_n$, ammonium dihydrogen phosphate ($NH_4H_2PO_4$), diammonium phosphate ($(NH_4)_2HPO_4$), boric acid (H_3BO_3), borax ($Na_2B_4O_7$·$10H_2O$), aluminium sulphate ($Al_2(SO_4)_3$), aluminium trihydrate ($Al(OH)_3$),ammonium sulphate ($(NH_4)_2SO_4$), ammonium borate ($(NH_4)_3BO_3$), urea (CH_4N_2O), guanidine phosphate ($CH_8N_3PO_4$), guanylurea phosphate ($C_2H_9N_4O_5P$) and other chemicals, or mixtures (Wiehn 1995, Mantanis 2002, Tsunoda *et al*. 2002, Pizzi and Mittal 2003, Sun *et al*. 2012, Mazela and Broda 2015, Mantanis *et al*. 2018). The fire retardants accelerate the formation of a char layer on the wood panel surface. Such FR additives for particleboard and OSB are used mostly in solid form, i.e. granulates having a particle size between 200 and 600 µm, while in MDF, hardboard, plywood, and some OSB, aqueous solutions are utilised. In MDF, these chemicals are applied to the fibres in the refiner blowline. Typically, such additives are formulated in water-based solutions having 50–65% content of active solids.

At present, polyphosphates along with monoammonium and diammonium phosphate as well boric acid and/or borax comprise the most frequent FR additives in the European MDF industry (Mazela and Broda 2015, Mantanis *et al.* 2018). However, upcoming changes in the European regulations may lead to the forbidding of boric acid from such wood applications. In general, fire retardants used in the wood-based panel industry are non-corrosive agents and halogen-free, since bromine- and chlorine-based compounds have been prohibited in the EU, from such industrial applications, with the REACH regulation (European Commission 2006). In Europe, fire-resistant MDF (FR-MDF) is produced by using exclusively MUF adhesives (12–16% melamine content) having a high molar ratio of formaldehyde to urea, i.e. higher than 1.20 (Alexandropoulos *et al.* 1998, Mantanis *et al*. 2018).

In addition, it has been suggested that boron-based chemicals should be used jointly with the main FR additives due to their smoke suppressing characteristics (LeVan and Winandy 1990, LeVan and Tran 1990, Wang *et al*. 2002). In specific, boric acid and disodium tetraborate decahydrate (borax) are

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mainly used in the industry as they reduce the flame spreading in the surface, once exposed to intense heat. Such additives can have a low melting point and build-up a glassy film layer upon the surface (Nussbaum 1988, Wang and Li 2004). Borax can eliminate the spread of flames, while boric acid enhances carbonisation; that is why they should be mixed when used (LeVan and Tran 1990, LeVan and Winandy 1990, Tondi *et al.* 2014). Further, in solid schemes, metal hydroxides such as magnesium hydroxide ($Mg(OH)_2$) and aluminium trihydrate (AlH_6O_3) are often employed in fire retardant systems to suppress smoke in the interim of the combustion (Barnes and Farrell 1978, Hashim *et al.* 2005, Wu and Yang 2010, Liang *et al.* 2017). The synergistic effect of borates with guanyl urea phosphate (GUP) has also been investigated in the recent years, proving to reinforce the fire resistance of cellulosic materials, also combined with low smoke properties (Gao *et al.* 2006, Liu *et al.* 2006, Guo *et al.* 2018).

According to the literature, in lignocellulosic materials when the temperature reaches approx. at 270°C, combustion behaviour is observed (Hakkarainen *et al.* 2005). Between 500°C and 800°C, carbonisation takes place. Combustion of solid wood or wood-based panels (i.e. fibreboards) can be dangerous, and influences habitable constructions and their content, e.g. furniture, doors, etc. In order to reduce the fibreboard flammability and provide safety, wood fibres should be sprayed with fire-retardant chemicals prior to the resination (Alexandropoulos *et al.* 1998, Liu *et al.* 2003). When FR additives applied, they retard combustion by releasing phosphoric acid esters, polysaccharides and water. Such compounds affect the dehydration reactions in wood (Grexa *et al.* 1999). Outstandingly, boron-based compounds are preferred in fibreboard production due to their thermal resistant characteristics (Tsunoda *et al.* 2002, Wang *et al.* 2004, Özdemir and Tutuş 2013). Recently, ammonium polyphosphate (APP) compounds have become the main fire retardant constituents because they are very efficient (Watanabe *et al.* 2009). In fact, APP compounds cause a carbon layer effect on the combustion behaviour. Such a layer blocks the access of oxygen and heat, which inhibits further combustion. Nonetheless, they have the disadvantage of being highly acidic and, additionally, lead to an increase of the amount of smoke. This is the reason why they have to be combined with other chemicals, namely smoke suppressants, such as potassium aluminium sulphate, borax, ammonium pentaborate, magnesium sulphate and guanidine sulphamate (White and Sweet 1992, Mantanis 2002, Wang *et al.* 2002, Dunky 2003, Wang and Li 2004, Mazela and Broda 2015). Such additives can have synergetic effects in respect to smoke properties as well as to hinder corrosive side effects into the core of wood panels.

Therefore, two aqueous FR additives were synthesised in this work, which mainly were composed of a mix of polyphosphates and borates and, to a lesser extent, of aluminium-containing reagents. Hence, the main objective of the study was to evaluate the fire and smoke properties of laboratory-made medium density fibreboard bonded with a melamine-urea-formaldehyde (MUF) resin, and to compare the fire efficiency of these additives versus that of a commercial highly effective FR product. The fire performance properties of fibreboard were assessed by using an in-house empirical test as well as the Cone calorimeter. Additionally, this work aimed at investigating the effects of FR treatments on the mechanical and physical properties of medium density fiberboard.

Materials and methods

Materials

Scots pine (*Pinus sylvestris* L.) wood fibres were obtained from an MDF mill. Fibres were screened to obtain fibre size between 0.5 and 1 mm. They were then oven dried at a temperature of 75°C for approx. 24 h to achieve approx. 7% moisture content. A melamine urea formaldehyde (MUF) resin was used as a binder. The properties of the MUF resin are as follows: F/U molar ratio: 1.30, melamine content: 12%, solid content: 64%, viscosity: 260 cps, gel time: 60 s, water tolerance: 1/0.8, and pH 9.25. No hardener was mixed with the binder in all cases, while 1% wax (dry on dry wood fibres) was applied in all MDF panels produced in the laboratory.

Fire retardants

Three fire retarding additives were used in this research work. First, Siriono® was obtained from a European MDF mill. In fact, fire retardant Siriono® is a halogen-free, colourless, low-viscosity ammonium phosphate – nitrogen based product which imparts superior fire retarding properties to lignocellulosic products like MDF and OSB (Siriono®: density 1.30 g/cm^3; solids content: 51%; pH: 6.95). It is composed primarily of polyphosphates, while its exact composition is proprietary.

An FR additive, named C7/2, was prepared in the laboratory as a halogen-free product. It is a low-viscosity agent based on ammonium polyphosphate (APP) and diammonium phosphate (DAP) along with borates like boric acid and borax, combined together at 18% addition on dry fire retardant chemicals, and also urea (C7/2: density 1.28 g/cm^3; solids content: 48%; pH: 6.00). Ammonium polyphosphate (APP, phase I) is an inorganic salt of polyphosphoric acid and ammonia, with short chains (<20), low polymerisation degree, with a content of P_2O_5>60%.

In addition, another aqueous fire retardant, named as C7/3, was investigated in the work. This is a halogen-free product of low-viscosity based also on APP and DAP together with borates like boric acid and borax (mixed together at a 20% addition on dry FR chemicals) as well as urea and to a small percentage an aluminium-based compound, namely potassium aluminium sulphate, known as alum (C7/3: density 1.28 g/cm^3; solids content: 48%; pH: 6.15).

The fire retardants were used as they were with no dilution. The FR addition level was the same, 12% (dry FR on dry fibre) in all cases, except for the control which was left untreated.

Fibreboard fabrication

The target board size and density of fibreboards were 350 × 350 × 10 mm^3 (length × width × thickness) and 760 kg/m^3, respectively. Air-dry fibres were placed in a laboratory scale mixer equipped with a spray gun. Initially, the wood fibres were sprayed with the aqueous fire retardant using an

Table 1. MDF sample dimensions for fire, physical, and mechanical tests.

Property	Dimensions (in mm)	Standard
Density	50 × 50	EN 323
Moisture content	25 × 25	EN 322
Internal bond (IB)	50 × 50	EN 319
Thickness swelling (TS)	50 × 50	EN 317
Water absorption (WA)	50 × 50	EN 317
Perforator (HCHO release)	25 × 25	EN ISO 12460-5
Gas analysis	400 × 50	EN ISO 12460-3
Fire test – reaction to fire	100 × 100	ISO 5660-1

airless spray gun which was attached on the top of the mixer. The fibres were repeatedly circulated in the 10 m long, circular tube-like mixer system. After a few minutes, with the mixer operating, MUF glue mix diluted with water at 50% solids was sprayed onto the fibres, for a period of approx. 5 min. After the uniform mixing, the moisture content of the impregnated and glued fibres varied between 14% and 16%. After that, the glued fibres were removed from the mixer. A small laboratory-scale shredder was used to separate the agglomerated fibres; this step was necessary before the air drying. Afterwards, the separated fibres were dried in a closed laboratory-scale flash drier, using injected hot air (85-90°C) for a period of ca. 5 min. This drying duration resulted in a suitable moisture content of the fibres, i.e. mat moisture after drying, 10–10.5%. The dried fibres were then removed and formed a fibre mat which was cold pre-pressed.

The pre-pressed mixture was finally hot pressed at a pressure of approx. 4.0 MPa, for a total press time of 2 min. For the untreated mixture, the press time was also 2 min. All treated and untreated fibres were pressed to 10 mm thickness, at a temperature of 200°C to remove excessive moisture from the fibres. A total number of 16 fibreboards were fabricated in this work. The fibreboards were then conditioned in a conditioning room (60 ± 5% RH and 23 ± 2°C) for three days, before they were trimmed for the fire, physical and mechanical tests. Sizes of fibreboards for each test are presented in Table 1, while the hot-press parameters for the laboratory-made boards are shown in Table 2.

Fire performance tested by the in-house method

Fire performance of the untreated and treated fibreboards was assessed using an in-house method. This involves the evaluation of weight loss and burnt length of the MDF specimens. In fact, samples measuring 30 cm in length and 5 cm in width, were first weighed to estimate their initial weights, and then were placed on a test gauze at butane flame, from a distance of 5 cm. The flaming angle was approx. 90°. The duration of flaming was 30 sec and the average weight loss and average mark length were recorded. The weight loss was estimated, after the specimens reached the ambient temperature.

The samples were burnt for 30 sec after ignition occurred on the samples. The samples were reweighed after the test,

Table 2. Hot press parameters for laboratory-made MDF.

Parameters	Value
Temperature	200°C
Pressure	4.0 MPa
Press time	12 sec/mm

and the burnt length on the sample surface was determined using an electronic calipre. The weight loss and the burnt length were determined using the following equations:

$$\text{Weight loss (\%)} = (W_i - W_a)/W_i \quad (1)$$

$$\text{Burnt mark length (mm)} = \text{burnt length run by the flame} \quad (2)$$

where W_i is the conditioned initial weight (g), and W_a is the conditioned weight after testing (g).

Cone calorimeter test

Fire performance of investigated samples was determined by the cone calorimeter (Fire Testing Technology Ltd., UK). Both the cone calorimeter and the testing procedure were in accordance with ISO 5660–1 (2015). Samples were loaded by heat flux of 50 kW/m^2 during the cone calorimeter test. Tests were repeated four times for each type of treatment (control, Siriono®, C7/2, C7/3), and the average values were calculated. The maximum average rate of heat emission (MARHE) was assessed from data measured by the cone calorimeter according to Zhang (2008). The flashover category was determined by a method suggested by Kokkala *et al.* (1993), which is based on data measured by the cone calorimeter.

Statistical analysis

Data from the fire tests were analysed using a computerised statistical program to perform an analysis of variance (ANOVA) and by carrying out the Duncan test at a $p \leq .05$ confidence level. Homogeneous groups with small letters were indicated with a superscript.

Results and discussion

Physical properties

As shown in Table 3, the thickness swelling and water absorption of produced fibreboards increased considerably after the

Table 3. Physical and mechanical properties of lab-made fibreboards.

	Type of FR treatment			
Property	Control	Siriono®	C7/2	C7/3
Density[a] (kg/m^3)	680	704	682	653
	(33)[c]	(43)	(45)	(42)
IB[a] (N/mm^2)	0.27	0.15	0.13	0.12
	(0.09)	(0.05)	(0.04)	(0.04)
2 h TS[a] (%)	3.4	8.2	8.4	7.2
	(0.4)	(2.9)	(1.2)	(1.0)
24 h TS[a] (%)	12.0	21.2	28.3	29.4
	(1.1)	(4.9)	(4.1)	(4.3)
2 h WA[a] (%)	10.7	21.7	23.0	22.4
	(1.0)	(3.6)	(3.6)	(2.7)
24 h WA[a] (%)	34.5	56.5	65.4	72.8
	(2.5)	(11.4)	(11.2)	(7.6)
Perforator[b] (mg/100 g)	72.4	8.5	4.8	4.4
Gas analysis[b] (mg/m^{2}h)	26.5	4.4	3.4	3.0

Note: IB: internal bond, TS: thickness swelling, and WA: water absorption.
[a]Mean of twelve (12) values;
[b]Mean of three (3) values;
[c]Values in parentheses are standard deviations.

treatment with the fire-retardant chemicals, as compared with the untreated panels.

In particular, the 2h-swellvalues of MDF panels increased from 3.4% (control) to 8.2% (Siriono®), 8.4% (C7/2) and 7.2% (C7/3). Similarly, untreated MDF panels showed a 24-h thickness swell value of 12.0%, while the FR treated panels exhibited much larger thickness increases, that is, 21.2% (Siriono®), 28.3% (C7/2) and 29.4% (C7/3). Obviously, the FR treatment with additive Siriono® had the least deleterious effect on thickness swelling. In any case, the overall effect of FRs on thickness swelling of the fibreboard panels was very significant ($p > .05$).

As revealed in Table 3, similar results were also found for the water absorption properties. Untreated MDF exhibited a 24 h water absorption value of 34.5%, while the FR treated panels showed higher WA increases, i.e. 56.5% (Siriono®), 65.4% (C7/2) and 72.8% (C7/3). The panels treated with Siriono® had the least deteriorating results as compared with the treatments of C7/2 and C7/3 FR additives.

It is known that thickness swell provides a measure of the dimensional stability of the fibreboards. Higher swelling values indicate a less stable wood panel. Thickness swelling can be influenced by several parameters such as wood species, panel density, resin type and its molar ratio, glue addition level, blending efficiency and pressing conditions (Kojima and Suzuki 2009). It has been reported that the internal bond has a direct relationship with thickness swelling (Febrianto *et al*. 2010). Evidently, in this study, the presence of polyphosphate salts in fibreboards have prevented strong links between the fibres, as the resin apparently did not have direct contact with the fibre surfaces, hence reducing the internal bond strength (Ayrilmis 2007), as seen in Table 3.

Regarding the perforator and gas analysis tests, it was observed that the formaldehyde release of the MDF panels was significantly decreased, i.e. at the E1 class level, after the addition of the polyphosphate-based FR additives. In particular, the fibreboard panels treated with Siriono®, C7/2 and C7/3 had Perforator formaldehyde content values of 8.5, 4.8 and 4.4 mg/100 g, respectively. In meanwhile, the control panels had a high formaldehyde release, i.e. 72.4 mg/100 g (EN ISO 12460–5 2016b). This large drop in the formaldehyde properties of the panels was anticipated, since it is known that all ammonium phosphate-based chemicals are very sturdy formaldehyde catchers in wood panels bonded with formaldehyde-based adhesives (Alexandopoulos *et al.* 1998, Dunky 2003). The effect of the investigated FRs on formaldehyde release of MDF panels was significant ($p > .05$). Similarly, the test results regarding formaldehyde release of treated MDF panels, as shown by the gas analysis method (EN ISO 12460-3 2016a) were very pronounced as well.

Internal bond strength

Internal bond (IB) strength is a fundamental indicator of the adhesive performance in wood-based panels. From the results of the study, it became apparent that the IB of the FR-treated fibreboards was inferior to that of the untreated (control). The mean IB value of the untreated fibreboards was 0.27 N/mm^2. The addition of polyphosphate-based fire retardants had a deleterious effect on the tensile strength properties of the fibreboards.

Table 4. Summary of ANOVA for the effects of different FRs.

	F-value		
Property	Siriono®	C7/2	C7/3
IB	2.54	0.77	1.35
Significance level	*	*	*
24 h TS	0.00047	0.00047	0.00011
Significance level	*	*	*
24 h WA	0.00031	0.00011	0.00004
Significance level	*	*	*

*Significance at 95%; IB: internal bond; TS: thickness swelling (24 h); WA: water absorption (24 h).

In specific, the internal bond strength of the panels treated with FRs such as Siriono®, C7/2 and C7/3 were, on the average, 0.15, 0.13 and 0.12 N/mm^2, respectively. This actually demonstrates a significant IB strength decrease of approx. 44%, 51%, and 55%.

Similar results were reported by Ayrilmis (2007) in a work on the fire-retardant treated MDF containing monoammonium and diammonium phosphates. IB strength losses found in the work can be attributed either to the chemical or mechanical changes in the wood cell-wall structure, or to the contamination of fibre surfaces by loosely adhering deposits of fire retardants in the glueline which interfered with the attainment of intimate fibre-to-fibre contact (Winandy 2001, Ayrilmis 2007).

A summary of ANOVA statistical results for the effects of selected FRs on the board properties like IB, 24 h TS, and 24 h WA is shown in detail in Table 4.

Weight loss and burnt length

Lower total weight loss implies higher resistance against thermal degradation of fire, and smaller burnt length indicates a better protection against flame spread. This test is empirical and gives visual observation and some useful indications (Figure 1).

Results of weight loss and burnt mark length, from the in-house FR test, for untreated and FR-treated fibreboards are

Figure 1. Some burnt MDF specimens after the in-house FR test (treated specimens; 1–2: control; 3–4: Siriono®; 5–6: C7/2; 7–8: C7/3).

Table 5. Fire performance of MDF panels treated with selected FR additives.

Type of treatment	Weight loss[a] (%)	Burnt mark length[a] (mm)
Control	2.88	11.25
Siriono®	1.63	9.40
C7/2	1.28	9.25
C7/3	1.37	9.75

[a]Mean value of six (6) specimens.

given in Table 5. The results indicated that the used FRs decreased the weight loss to some extent, while the burnt mark length was somewhat reduced.

The weight loss of MDF was decreased from 2.88% (untreated), to 1.63% (Siriono®), 1.28% (C7/2) and 1.37% (C7/3). The burnt mark length also lowered from 11.25 mm (control) to 9.40, 9.25 and 9.75 mm, respectively. From this empirical test, apparently, the FR treatment with C7/2 chemical gave the best FR results, in comparison with the other two FR treatments.

The active ingredient of agent C7/2 is phosphorous (P), combined with nitrogen (N), and like most phosphorous-containing fire retardants, phosphorus works out by enhancing char formation on the sample surface. The protection mechanism of the FR is as same as other phosphorous-based fire retardants such as monoammonium and diammonium phosphates which provide a protective layer which subsequently reduces flame spread (Izran *et al.* 2010). Both C7/2 and C7/3 in this work are enhanced with a very high percentage of borates (boric acid and borax). Previous laboratory tests, in particleboard panels, indicated that Siriono® was efficient so as to improve flame spread classification to the highest European class B (İstek and Özlüsoylu 2016).

Combustion performance

The heat release rate (HRR) and the total heat release (THR) are shown in Figure 2. All samples showed two peaks of the heat release rate. First peaks occurred closely (15–35 sec) after ignition, and second peaks occurred during simultaneous flame and flameless (glowing) combustion. This trend corresponds with the typical behaviour of wood based materials as shown by White and Sumathipala (2013). The control samples exhibited significantly higher first and second heat release rate peaks, in relation to the samples treated with the investigated fire retardants (Figure 2).

Figure 3 illustrates the smoke production rate (per unit of sample area) and the total smoke release (per unit of sample area) from the fibreboard samples. The smoke production rate was similar to that of heat release rate, e.g. two peaks were shown. The shape and time to peaks roughly corresponded to the heat release rate peaks. Both the first and second peaks of the smoke production rate of control sample were significantly higher than the peaks of samples treated with the fire retardants (Figure 3). Moreover, the samples treated by the fire retardants showed roughly five times less total smoke release than control samples (Figure 3). The differences between smoke production from the control sample and FR-treated samples are obvious, even without a statistical analysis (e.g. ANOVA).

The mass loss and the mass loss rate, called specific mass loss rate, are shown in Figure 4. Comparison of Figures 2 and 4 proved that the specific mass loss rate and heat release rate had very similar trends. This observation is in accordance with the work of Martinka *et al.* (2018). The

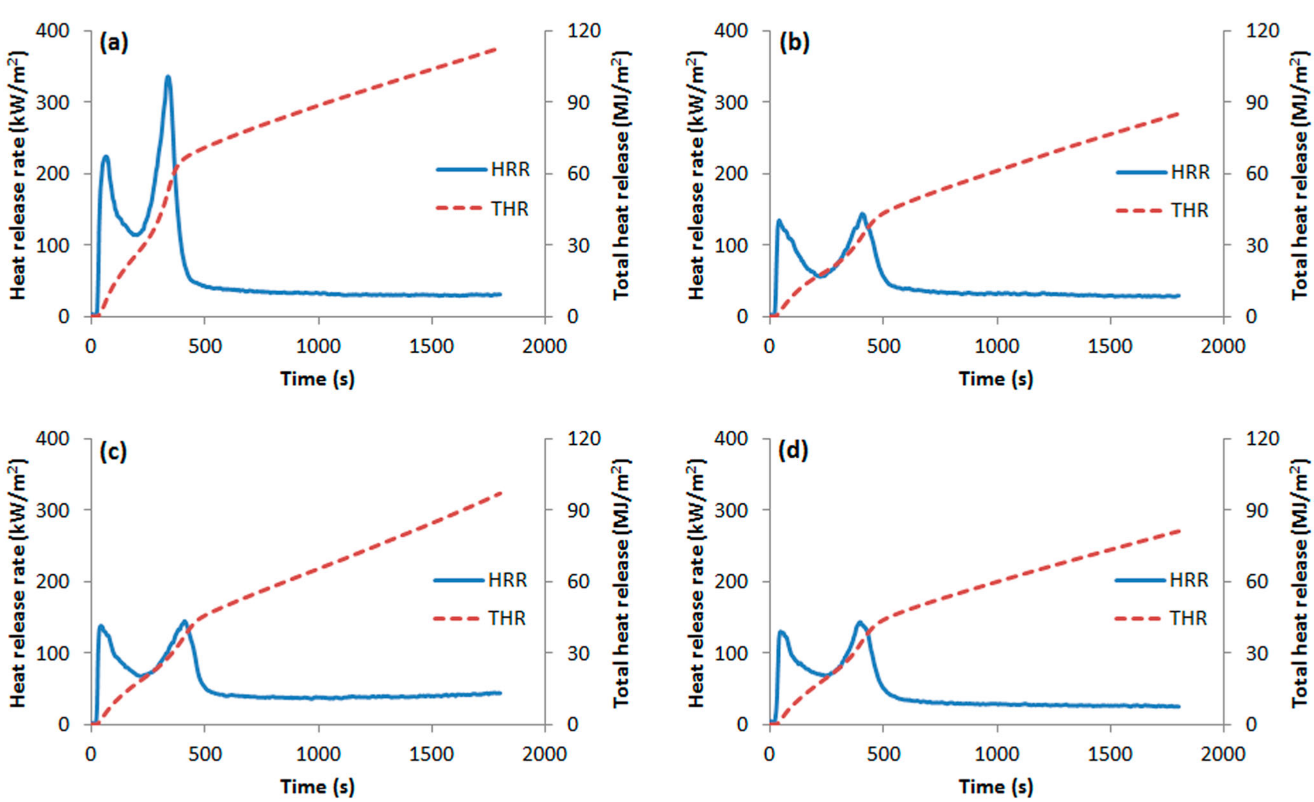

Figure 2. Comparison of heat release rate and total heat release of FR-treated and untreated MDF samples: (a): control; (b): Siriono®; (c): C7/2; (d): C7/3.

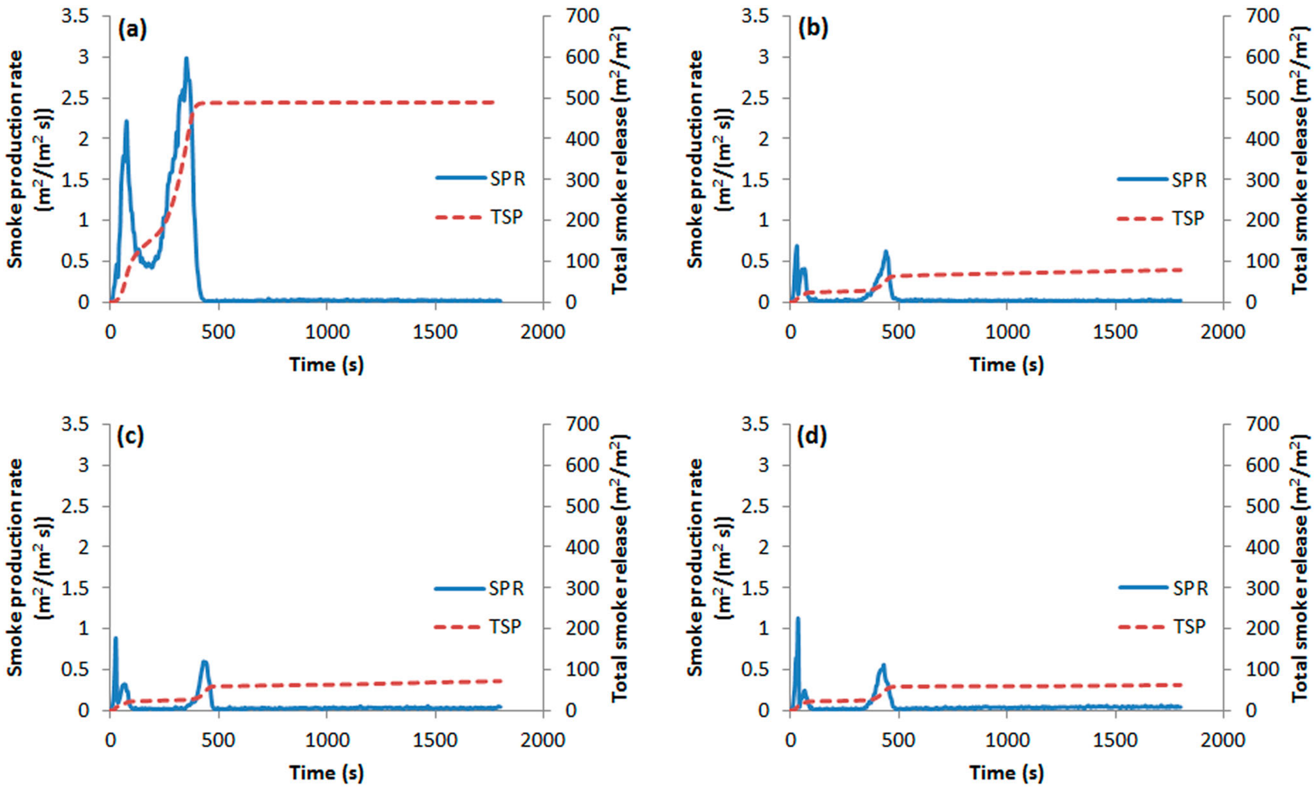

Figure 3. Comparison of smoke production rate (SPR) and total smoke release (TSR) of FR-treated and control MDF samples: (a): control; (b): Siriono®; (c): C7/2; (d): C7/3.

cause of dependence of the heat release rate on the specific mass loss rate is the fact that the released heat is determined by specific mass loss rate and the effective heat of combustion; i.e. when the effective heat of combustion is constant, the heat release rate is the only function of the specific mass loss rate. The differences between mass loss of control sample and treated samples are very apparent even without a statistical test (e.g. ANOVA).

Table 6 shows some important fire performance parameters such as peak heat release rate (peak HRR), total heat release (THR) and total smoke production (TSP), in detail. It is apparent that these parameters were improved in FR-treated panels to a significant extent. In specific, for Siriono®, the peak HRR, THR and TSP of treated MDF panels in the cone calorimeter were approx. 62.2%, 24.5%, and 83.6% lower as compared with those of untreated fibreboards. Almost equivalent FR results have been obtained with the other two fire-retardant chemicals. Noticeably, the FR C7/3 resulted in much better TSP properties. Indeed, as shown in Table 6, C7/3 resulted in the lowest total smoke production, as compared with C7/2 and Siriono®, a difference which was statistically significant. This should be attributed to the addition of alum, which obviously imparts higher smoke suppressing properties to the cellulosic materials, like fibreboards, due to the presence of aluminium (Garba *et al.* 1994, Onnegbu and Ejimotor 2011).

Table 6. Fire performance parameters of investigated MDF samples.

Treatment	Peak HRR (kW/m^2)	THR (MJ/m^2)	TSP (m^2)
Control	408 (17)[a]	114(7)	4.27 (0.31)
Siriono®	154 (12)	86 (6)	0.70 (0.05)
C7/2	157 (10)	97 (9)	0.63 (0.07)
C7/3	159 (11)	81 (9)	0.55 (0.06)

[a]Values in parentheses are standard deviations.

Additionally, APP although is an excellent FR, it catalytically generates lots of smoke and poisonous gases during combustion. Thus, it should be combined with other chemicals, such as borates and/or aluminium-containing compounds or other, to reduce the smoke release and air pollution.

From these results, it seems that APP and borates together have synergistic effects on the fire performance and smoke-suppression in fibreboards (MDF); i.e. boric acid and borax mixed together in an ammonium polyphosphate solution can result in to efficiently retard flame, to diminish fire intensity and to decrease largely the noxious smoke (CO) release.

In addition, the time to ignition, first peak of heat release rate, time to heat release rate first peak and MARHE of investigated MDF samples are demonstrated in Table 7.

Data in Table 7 proved that MDF treated by fire retardants had a significantly lower first peak of heat release rate and MARHE, than the untreated MDF. The impact of treatment on the time to ignition is only negligible, from the technical point of view. On the contrary, the treated MDF showed a shorter time to the first peak of heat release rate (Table 7). In Table 8, data have been analysed by the analysis of variance (ANOVA) at a $p \leq .05$ confidence level, to reveal any possible impact of treatment of MDF by the investigated fire retardants on their fire performance.

Data in Table 8 displayed that there were statistically significant differences between investigated MDF samples (treated and untreated) concerning the time to ignition, first peak of heat release rate, time to first peak of heat release

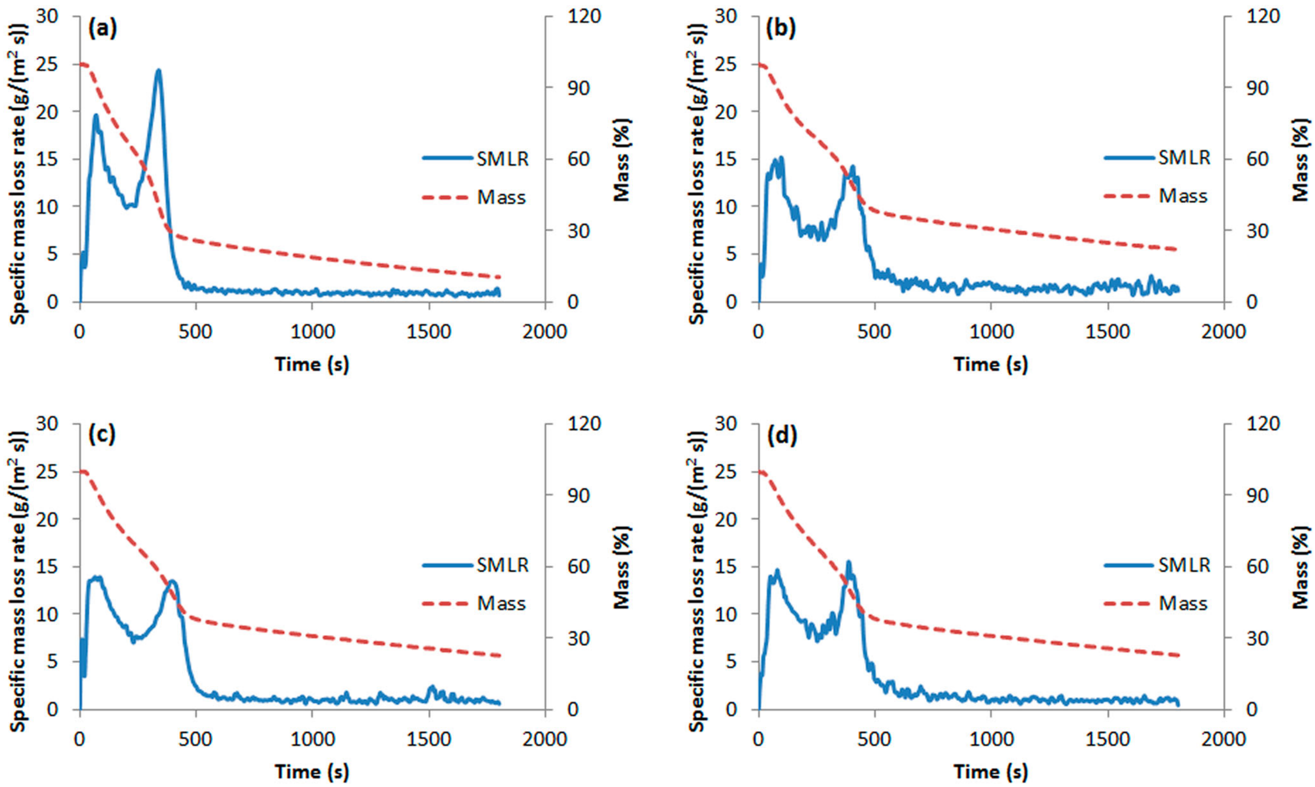

Figure 4. Comparison of mass loss and specific mass loss rate of FR-treated and untreated MDF samples: (a): control; (b): Siriono®; (c): C7/2; (d): C7/3.

Table 7. Fire characteristics of investigated MDF samples.

Treatment	Time to ignition (s)	First peak of HRR (kW/m^2)	Time to first peak of HRR (s)	MARHE (kW/m^2)
Control	32 (3)[a]	226 (12)	63 (7)	169 (8)
Siriono®	29 (3)	135 (4)	40 (4)	92 (9)
C7/2	28 (2)	139 (5)	43 (6)	95 (3)
C7/3	35 (4)	133 (6)	48 (6)	91 (5)

[a]Values in parentheses are standard deviations.

Table 9. Duncan's test revealing the impact of FR treatment on time to ignition.

Sample (-)	Duncan's p value (–)			
	Control	Siriono®	C7/2	C7/3
Control	–	0.26879	0.12318	0.15762
Siriono®	0.26879	–	0.57284	0.02539
C7/2	0.12318	0.57284	–	0.01041
C7/3	0.15762	0.02539	0.01041	–

rate and MARHE. Data in Table 8 did not reveal whether there were statistically significant differences between fire performances of treated MDF samples. Therefore, obtained data were tested by ANOVA post-hoc test (Duncańs test). Results of the Duncan's test are shown in Tables 9–12.

Indeed, it appears that the time to ignition of FR-C7/3 treated samples is statistically significant higher than the time to ignition of Siriono® and C7/2 treated MDF samples (Table 9). Data in Tables 10–12 prove that the first peak of HRR, time to first peak of HRR and MARHE of treated MDF samples are statistically significant lower than the first peak of HRR, time to first peak of HRR and MARHE of control samples. Therefore, the treatment of MDF with the investigated fire retardants reduced the first peak of HRR (positive effect), time to first peak of HRR (negative effect) and the MARHE (positive effect). The impact of fire treatment on the time to first peak of HRR is statistically significant, but it is not significant from the technical point of view.

At last, Table 13 illustrates the time to flashover of treated MDF samples. The time to flashover was calculated according to the method of Kokkala *et al.* (1993), which is presently considered as very reliable (Martinka *et al.* 2018). This method allows calculation of time to flashover in intervals <0–2 min, <2–10 min, <10–20> min, and without flashover. As a matter of fact, there were actually no significant differences between times to flashover of the FR treated MDF panels.

Table 8. ANOVA results revealing the impact of MDF treatment on fire performance.

ANOVA parameters (–)	Time to ignition (s)	First peak of HRR (kW/m^2)	Time to first peak of HRR (s)	MARHE (kW/m^2)
F	4.10	154	11.47	141
F_{crit}	3.49	3.49	3.49	3.49
p	0.032	0.000000000763	0.000773	0.00000000123

Table 10. Results of Duncańs test revealing the impact of FR treatment on first peak of HRR.

Sample (–)	Duncan's p value (–)			
	Control	Siriono®	C7/2	C7/3
Control	–	0.00010	0.00017	0.00007
Siriono®	0.00010	–	0.45177	0.70420
C7/2	0.00017	0.45177	–	0.28858
C7/3	0.00007	0.70420	0.28858	–

Table 11. Results of Duncan's test revealing the impact of FR treatment on time to first peak of HRR.

Sample (–)	Duncan's *p* value (–)			
	Control	Siriono®	C7/2	C7/3
Control	–	0.00034	0.00070	0.00405
Siriono®	0.00034	–	0.56364	0.11510
C7/2	0.00070	0.56364	–	0.25788
C7/3	0.00405	0.11510	0.25788	–

Table 12. Results of Duncan's test revealing the impact of FR treatment on MARHE.

Sample (–)	Duncan's *p* value (–)			
	Control	Siriono®	C7/2	C7/3
Control	–	0.00010	0.00017	0.00007
Siriono®	0.00010	–	0.59019	0.70532
C7/2	0.00017	0.59019	–	0.38846
C7/3	0.00007	0.70532	0.38846	–

Table 13. Time to flashover of investigated samples.

Sample (–)	Time to flashover (min)
Control	2–10
Siriono®	2–10
C7/2	2–10
C7/3	2–10

Conclusions

The fire retardants used in this work were effective in improving the fire performance of MDF by reducing thermal degradation as well as heat release properties. Moreover, the synergistic effect of APP, boric acid and borax led to the effective fire and flame retardancy of MDF panels tested.

The additives applied in the work imparted a slight brown colouration on treated MDF panels. As shown, there have been drastic increases in the thickness swell and water absorption properties caused by the incorporation of fire retardants in the fibreboards. IB of the panels was negatively affected by all of the fire retardants used, up to 55%. Noticeably, the treatment with Siriono® resulted in the least deleterious effects in relation to the IB deterioration. This drastic strength reduction in MDF treated with the polyphosphate-based fire retardants was possibly caused by a combination of chemical changes in the fibre cell-wall structure, or the interference of the deposits of FRs with the bonding lines.

The MDF samples treated with selected fire retardants, namely Siriono®, C7/2, C7/3, had showed significantly lower peaks of HRR, time to first peak of HRR, MARHE, peaks of smoke production rate, total smoke release and specific mass loss rate. On the other hand, the impact of treatment of MDF samples with fire retardants on time to ignition was ambiguous; Siriono® and C7/2 additives resulted in lower time to ignition, while C7/3 resulted in higher time to ignition than the control sample.

On the contrary, the treatments with the investigated fire retardants exhibited no effects on the time to flashover. The decrease of time to first peak of HRR and time to ignition as a consequence of treatment by investigated fire retardants was not significant, for technical practice. On the other hand, the reduction of the first peak of HRR, MARHE and total smoke release as a consequence of treatment by investigated fire retardants was indeed very significant.

Noticeably, the small presence of aluminium potassium sulphate (alum) in the FR additive C7/3 resulted in the highest decrease of the total smoke production (TSP), as compared with the results with the chemical additives Siriono® and C7/2. In overall, the investigated fire retardants have shown positive effects on the level of fire safety of medium density fibreboards.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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