3rd International Conference on Bio-Based Building Materials

June 26th - 28th 2019
Belfast, UK

# FORMULATION OF NOVEL FIRE RETARDANT ADDITIVES FOR BIOBASED INSULATION MATERIAL

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**Abstract**

This study deals with the development of novel fire-retardant formulations to reduce the flammability of a low density rigid insulation panel made from hemp shiv glued with a thermosetting bio-binder. The objective is to identify possible substitutes to conventional fire-retardants, which are free from ammonium salts or boron compounds. The effect of the different treatments on the thermal decomposition of hemp shiv was analyzed by TGA/DA. The fire reaction of the insulation panel made of treated hemp shiv and bio-binder was characterized using the standardized cone calorimeter test. Two conventional treatments are used as references: a commercial ammonium phosphate/sulfate flame-retardant and a commonly used flame-retardant composition based on boric acid. Results showed that magnesium sulfate heptahydrate, phosphoric acid, sulfuric acid, functionalized silica particles and a combination of these could provide better fire retardancy effect than the conventional treatment based on boric acid. However, some treatments were not compatible with the selected panel formulation because they hindered the thermosetting binder polymerization leading to poor mechanical properties.

**Keywords:**

Bio-based materials, hemp shiv, insulation, fire retardants

## 1 INTRODUCTION

This study is part of the ISOBIO project whose objectives are to develop high performances and low embodied energy bio-based materials for buildings construction. In recent results, a new low density rigid panel from hemp shiv has been developed, using a bio-based thermosetting binder. The hemp shiv panel having a density between 170 kg/m$^3$ and 250 kg/m$^3$ offers a very low thermal conductivity, between 0.050 W/m.K and 0.060 W/m.K which makes this material an ecofriendly solution for building insulation [Colson 2017]. However, due to its cellulosic chemical nature and its low-density, this material remains highly flammable. Consequently, its use may be hindered in some building applications.

A solution to overcome this issue would be to use traditional fire retardant additives based on ammonium salts or boron compounds. However, these fire retardants already led to toxicity controversy. Indeed, ammonia releases in buildings were detected when using ammonium phosphate/sulfate salts. More, boron compounds are classified as CMR class 2 according to REACH regulation [ECHA 2010].

Despite the toxicity issues, materials manufacturer still uses these fire retardants because no effective substitutes are available at a competitive cost. Therefore, this study aims to identify novel fire retardant formulations which are less toxic, remain accessible and efficient. Several innovative solutions were identified in the literature. Shutt [Shutt 2017] patented a solution to treat cellulose insulation without ammonium salt and boron compounds using a combination of a strong acid with magnesium sulfate or calcium sulfate. Results showed that 3% of sulfuric acid or phosphoric acid combined with 6-12% of magnesium sulfate heptahydrate or a combination magnesium sulfate/calcium sulfate allowing to reach Euroclass B or C. Magnesium sulfate heptahydrate is an interesting solution because it is nontoxic and low cost. Elvira Leon *et al.* [Elvira-León 2016] observed improved fire retardancy effect on different species of wood impregnated with magnesium sulfate hydrate. A delayed ignition and a reduction of the heat release rate were observed which could be explained by the double action: in the condensed phase by endothermic decomposition (cooling effect) and in gas phase by dilution of flammable gases with water vapour.

Another alternative would be to use inorganic materials acting as a heat shield to substrate (condensed phase) beneath, by increasing the thermal mass of the materials and increase the time before the onset of pyrolysis. Heat-shielding effect of silica layers has been proven on polymers [Hshieh 1998; Kashiwagi 2000; Mingzhu 2013]. Branda *et al.* observed a reduction of mass loss rate as measured by thermogravimetric analysis when hemp fabrics were impregnated with sodium silicate [Branda 2016]. Such work suggests that bio-based materials such as hemp shiv could be treated with silica-derived compounds. It would be expected to improve their fire performances, which forms part of the work described in this study. Silica particles deposited on hemp shiv according to the procedure described by Bourebrab et *al.* [Bourebrab 2017] already proved to delay biodegradation of the bio-materials. It is thus expected to witness a reduction in the thermal degradation of hemp shiv as well provided by the silica particles.

These formulations will be tested on the novel rigid hemp shiv insulation panel and their effectiveness will be compared with two traditional fire retardant treatments based on ammonium salts and boron compounds.

## 2 MATERIALS AND METHODS

### 2.1 Materials

A commercial building grade of hemp shiv (Biofibat®, Cavac Biomatériaux, France) was used. The bio-based thermosetting binder was formulated using bio-based water soluble macromolecules (matrix), residue from food industry, and a crosslinker [Colson 2017]. Phosphoric acid concentrated at 85% and sulfuric acid concentrated at 98% were supplied by Sigma Aldrich Chemical, France. The boric acid used was a commercial grade TG Granular Optibor® commercialised by the company Rio Tinto. EPSO TOP® Magnesium sulfate heptahydrate was supplied by K+S KALI GmbH. SYNTHRO-NYL SNP 1813s® is a commercial flame retardant solution based on ammonium sulfate/ammonium phosphate supplied by SYNTHRON, France, which rational composition is not exactly known. Silica particles of 110 nm diameter were synthesised at TWI Ltd. UK via the Stöber process as described by Bourebrab *et al.* [Bourebrab 2018]. They were functionalised with the hydrophobic agent n-propyl trimethoxysilane in order to prevent aggregation according to Bourebrab *et al.* [Bourebrab 2017].

### 2.2 Fire retardant treatments

Solid additives were solubilised in water before being blended with hemp shiv. Tab. 1 presents the treatment formulations. Boric acid and magnesium sulfate heptahydrate were dissolved in water until reaching 4 wt% and 20 wt% of solid contents in solution respectively. Sulfuric acid and phosphoric acid solution were diluted to obtain a 10 wt% concentrated solution. The commercial flame retardant SYNTHRO-NYL SNP 1813s® supplied as a 50 wt% solution was diluted to 25 wt%. Functionalised silica particles were produced as a 7 wt% dispersion and used as such. Flame retardant additives are added to the hemp shiv in a laboratory blender SAMA by batch mixing as illustrated in Fig. 1. 500 g of hemp shiv are treated per batch and the action is repeated until 4 kg of hemp shiv are treated per formulation. When used in combination with other chemicals, magnesium sulfate heptahydrate solution was always added in second. The mixing time was set to 3 min for each addition.

*Tab. 8: Hemp shiv treatment composition in wt%*

| Treatment | Hemp shiv | Sulfuric acid (SA) | Phosphoric acid (PA) | Functionalised silica particles (FSP) | Boric acid (BA) | Magnesium sulfate Heptahydrate (MSH) | Commercial N/P flame retardant |
|---|---|---|---|---|---|---|---|
| **A Control** | 100 | - | - | - | - | - | - |
| **B 10MSH** | 90 | - | - | - | - | 10 | - |
| **C 20MSH** | 80 | - | - | - | - | 20 | - |
| **D 3SA-10MSH** | 87 | 3 | - | - | - | 10 | - |
| **E 3PA-10MSH** | 87 | - | 3 | - | - | 10 | - |
| **F 3FSP-10MSH** | 87 | - | - | 3 | - | 10 | - |
| **G 3BA-10MSH** | 87 | - | - | - | 3 | 10 | - |
| **H 13Commercial FR** | 87 | - | - | - | - | - | 13 |

*Fig. 7: Aggregates and additives mixing*

### 2.3 Thermogravimetric and thermodifferential analyses (TGA/TDA)

Treated hemp shiv were micronised using a laboratory knife mill (retsch ZM 200) and calibrated with a grid of 0.5 mm. The powder obtained was analysed by thermogravimetric and thermodifferential analyses (Perkin-Elmer Pyris-Diamond thermal analyzer). The samples were heated from 25°C to 900°C at 10°C/min rate under nitrogen atmosphere. The TDA evaluates the difference of temperature between the sample and a platinum reference exposed to the same heating conditions. The difference of temperature allows to highlight endothermic and exothermic reactions due to sample composition.

### 2.4 Hemp shiv panel manufacture

Panels were manufactured using the method described by Colson *et al.* [Colson 2017]. Treated hemp shiv were mixed with a biobased thermosetting binder. Panels were produced by thermopressing hemp shiv/binder mix at 190°C for 15 min using an hydraulic hot plates press. The density of the panel was controlled by adjusting the weight of material inserted in the mould (dimensions 600x600x50 mm$^3$). After pressing, the panel was removed from the press, cooled at air for 10 min and the mould was removed. Each panel was cut to produce three samples (dimensions 100 mm x100 mm x 50 mm) for cone calorimeter tests.

### 2.5 Cone calorimeter test

The cone calorimeter allows the estimation of the flammability of a material. This experiment was carried out at the University of Edinburgh on a Mettler-Toledo apparatus, equipped with a gas analyser, following the procedure described in the standards [ASTM 2017]. Common insulation materials, such as isocyanurate foams typically exhibit a critical heat flux (heat required for spontaneous ignition) between 12 kW/m$^2$ and 15 kW/m$^2$ [Hidalgo-Medina 2015], whereas smouldering ignition of hemp-lime composites can occur below 10 kW/m$^2$ [McLaggan 2016]. The heat flux chosen in this study was thus set above that of smouldering ignition of hemp-derived composites, and similar to that of competition insulation materials. Samples of dimensions 100 mm x 100 mm x t (< 50 mm) were thus exposed to a constant radiant heat flux of 15 kW/m$^2$ provided by the conical heater during 40 min. Under heat exposure, flammable gases were released and ignited with a 10000 V spark (piloted ignition). The mass losses of the samples were recorded and the concentrations of the combustion gases were monitored by the gas analyser located in the exhaust duct. The mass loss rate was obtained from the recorded measurement of mass loss throughout the test, whilst the heat release rate was calculated from the concentration of $O_2$, according to Janssens (oxygen consumption method) [Janssens 1991].

## 3 RESULTS AND DISCUSSION

### 3.1 TGA-TDA results

*TGA on loose untreated hemp shiv*

Fig 2. illustrates the TGA-TDA of an untreated hemp shiv. A weight loss of 9 wt% associated with an endothermic pic occurred between 25°C and 105°C which corresponds to water evaporation. A steady state was observed between 105°C and 220°C, which means that no thermal degradation occurred. An important weight reduction from 90 wt% to 34 wt% occurs between 220°C and 370°C. The heat flow shows that this weight loss refers to two sets of exothermic reactions.

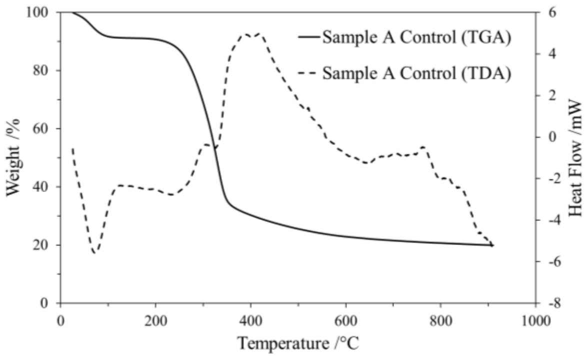

*Fig. 8: TGA/TDA of loose untreated hemp shiv*

The first, occurring from 220°C to 330°C is expected to represent the thermal degradation of hemicelluloses, whereas the second from 330°C to 420°C that of cellulose, which concurs with results from Yang *et al.* [Yang 2007].

*TGA-TDA of Magnesium Sulfate Heptahydrate*

Fig. 3 illustrates the thermogravimetric and thermodifferential analysis of magnesium sulfate heptahydrate (Epson salt). The weight loss started at 55°C and ended after 350°C. After 350°C, the residual weight fraction was stabilised at 49.3%. The thermo-differential analysis showed that each weight loss was associated with an endothermic reaction. Six distinct endothermic reactions were observed at 65°C, 103°C, 126°C, 160°C, 185°C and 260°C respectively. The corresponding residual weight after each endothermic peak was illustrated Fig. 3).

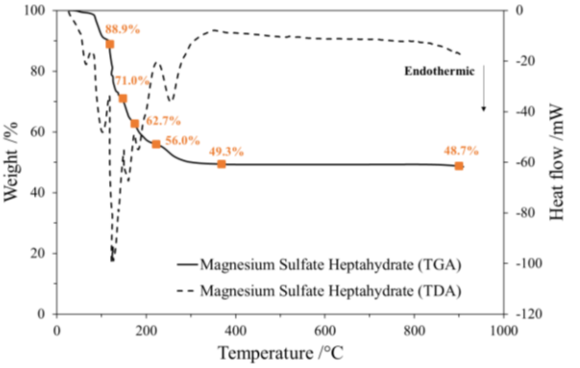

*Fig. 9: TGA/TDA of magnesium sulfate heptahydrate*

*Tab. 9: Theoretical molecular weight of magnesium sulfate hydrates and residual weight fraction*

| Hydrate form | Molecular weight* (g/mol) | Theoretical residual weight fraction** |
|---|---|---|
| $MgSO_4.7H_2O$ | 246.473 | 100.0% |
| $MgSO_4.6H_2O$ | 228.458 | 92.7% |
| $MgSO_4.5H_2O$ | 210.443 | 85.4% |
| $MgSO_4.4H_2O$ | 192.428 | 78.1% |
| $MgSO_4.3H_2O$ | 174.413 | 70.8% |
| $MgSO_4.2H_2O$ | 156.398 | 63.5% |
| $MgSO_4.1H_2O$ | 138.383 | 56.1% |
| **Anhydrous** $MgSO_4$ | 120.368 | 48.8% |

They are close to the theoretical molecular weight of the hydrate as illustrated in Tab. 2. Therefore, each weight loss corresponds to magnesium sulfate crystallised water molecule evaporation and the sample stabilisation at a weight fraction of 49.30% means that the magnesium sulfate reached its anhydrous form. These results were in accordance with the observation of Elvira- León *et al*, explaining the fire retardancy behaviour of magnesium sulfate heptahydrate by endothermic decomposition before cellulose pyrolysis and water vapor release. [Elvira-León 2016].

*TGA of loose treated hemp shiv*

Fig. 4.a shows that samples B and C treated respectively with 10 wt% and 20 wt% of magnesium sulfate have a decomposition profile similar to the untreated sample A. Tab. 3 shows that, for both treatments, the temperature of onset pyrolysis ($T_{onset}$) was slightly increased by 15°C when compared to the untreated sample.

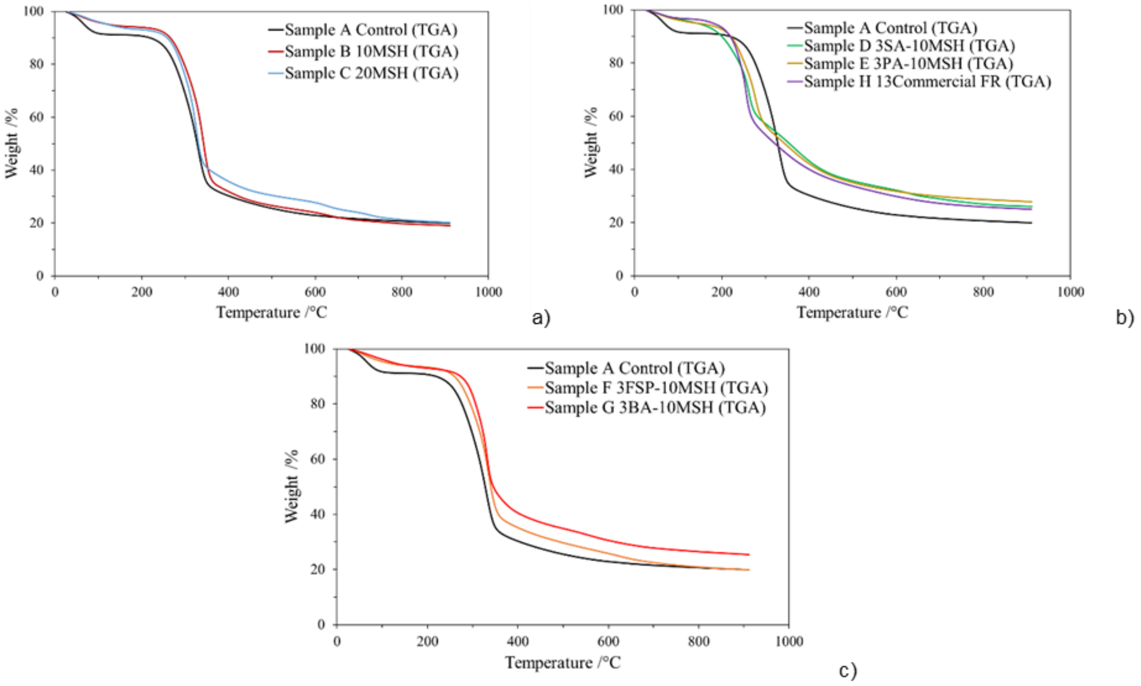

*Fig. 10 : TGA of loose untreated and treated hemp shiv. (MSH: Magnesium sulfate heptahydrate, SA: sulfuric acid, PA: Phosphoric acid, BA: Boric Acid, FSP: Functionalised Silica Particles, Commercial FR: Commercial flame retardant)*

This could mean that magnesium sulfate heptahydrate improves the thermal stability of hemicelluloses. It could be explained by a divalent metal crosslinking of hemicelluloses by $Mg^{2+}$ ions. Yin obtained a crosslinked alginate hydrogel by $Mg^{2+}$ ion [Yin 2015]. However, the maximum degradation rate (MDR) of the two samples B and C occurred respectively at 341°C and 328°C, which are in the same range as the untreated sample ($T_{MDR}$ at 328°C). This suggests that magnesium sulfate did not affect the thermal stability of cellulose.

Fig. 4.b shows a comparison between the untreated sample and samples D, E and H, corresponding respectively to the hemp shiv treated with 3 wt% of sulfuric acid and 10 wt% of magnesium sulfate, 3 wt% of phosphoric acid and 10 wt% of magnesium sulfate and, 13 wt% of commercial ammonium phosphate/sulfate flame retardant. Their thermal decomposition (in the condensed phase) followed a similar behaviour to that of the untreated. Indeed, Tab. 3 shows that treatments D, E and H displayed $T_{onset}$ at 183 °C, 206°C and 196°C respectively and their $T_{MDR}$ occurred respectively at 260°C, 275°C and 253°C. The $T_{onset}$ and the $T_{MDR}$ of the untreated sample were respectively 236°C and 328°C. The residual weight of the three treated samples at 300°C was between 53.01 wt% and 57.17 wt% but 68.89 wt% for the untreated one. However, at the 430°C, the residual weights of samples D,E and H, were measured between 37.64 wt% and 39.92 wt%, which are higher than the residual weight of the untreated sample (28.62 wt%).

This behaviour can be explained by the well-known “charring theory” of phosphate flame retardant. Nitrogen and phosphate are combined to provide a synergic flame retardancy effect. Under thermal decomposition, nitrogen compounds decompose into non-combustible gas and dilute the flammable gas phase. The decomposition of the nitrogen compound occurring around 150°C in the case of low molecular weight ammonium phosphate/sulfate also leads to the formation of phosphoric acid or sulfuric acid, which affects the reactions in the condensed phase. The acid modifies the pyrolysis reaction of lignocellulose molecules by anticipating the decomposition and catalysing the dehydration reaction resulting in the formation of carbon to carbon double bonds and charring. This reaction leads to the formation of char

*Tab. 10 : Temperature of onset pyrolysis ($T_{onset}$); temperature of maximum degradation rate ($T_{MDR}$) and mass residue. (The temperature of 300°C, 430°C and 600°C were defined arbitrary to highlight the different decomposition behaviours between samples)*

| Sample | $T_{onset}$ /°C | $T_{MDR}$/°C | Mass residue/% | | |
|---|---|---|---|---|---|
| | | | At 300°C | At 430°C | At 600°C |
| **A Control** | 236 | 328 | 68.89 | 28.62 | 22.90 |
| **B 10MSH** | 253 | 341 | 79.15 | 29.69 | 24.00 |
| **C 20MSH** | 251 | 324 | 75.59 | 33.52 | 27.74 |
| **D 3SA-10MSH** | 183 | 260 | 57.17 | 39.92 | 32.19 |
| **E 3PA-10MSH** | 206 | 275 | 56.54 | 39.25 | 31.81 |
| **F 3FSP-10MSH** | 249 | 335 | 77.83 | 33.18 | 25.86 |
| **G 3BA-10MSH** | 270 | 329 | 83.15 | 38.31 | 30.59 |
| **H 13Commercial FR** | 196 | 253 | 53.01 | 37.64 | 29.87 |

instead of laevoglucose compounds which are responsible of the flammable gas formation. [Huang 1975 ; Mngomezulu 2014].

As regards samples D and E, treated respectively with sulfuric and phosphoric acid without ammonium salt, the effect of the treatments on the decomposition of hemp shiv seemed similar to the treatment of sample H which was made with commercial flame retardant with ammonium salt. However, due to the nature of the TGA-TDA test, the effectiveness of these treatments as flame retardant cannot be confirmed.

Fig. 4.c illustrates the decomposition profile of samples F and G, corresponding to the hemp shiv treated with 10 wt% magnesium sulfate and either functionalised silica particles or boric acid. The two treatments did not affect significantly $T_{MDR}$. Indeed, the $T_{MDR}$ of samples F and G occurred at 335°C and 329°C respectively, which is close to the $T_{MDR}$ of the untreated sample. However, $T_{onset}$ increased for both treatment when compared to the untreated sample, from 236°C (sample A) to 249°C (sample F) and 270°C (sample G). The $T_{onset}$ of sample F is close to that of samples B and C, made from magnesium sulfate heptahydrate only, which suggests that this increase is only due the presence of magnesium sulfate, and the silica particles did not affect the thermal stability. In the literature, it is believed that silica particles act in the condensed phase through a physical fire retardancy mechanism by forming protective layer at the material surface which protects the material from the heat source [Mngomezulu 2014]. In this case, there is no chemical reaction occurring during thermal decomposition which explains that the decomposition profile is similar to the sample B treated with 10% of magnesium sulfate heptahydrate.

For sample G containing boric acid and magnesium sulfate heptahydrate, $T_{onset}$ is higher than samples B and C containing only magnesium sulfate heptahydrate. These results mean that boric acid improves the thermal stability of hemicelluloses. Uner *et al.* obtained similar results on wood treated with different proportion of boric acid [Uner 2016]. However, no explanations were given. Uddin *et al.* observed also similar results on chitosan and cellulose nanofibril treated with boric acid [Uddin 2017]. This stability increase may be explained by a complexation reaction between polysaccharides and boric acid [Pappin 2012; Wang 2004].

In the literature, it is also explained that boric acid acts in the condensed phase similarly to phosphate by promoting cellulose and hemicellulose dehydration and anticipating pyrolysis. However, the anticipated pyrolysis was not clearly visible on the TGA curve (Fig. 4.b). It is possible that in our case the boric acid content was too low to observe pyrolysis anticipation. However, it is clear that it affected the char residue as the final residue at 900°C was similar to the hemp shiv treated with commercial ammonium phosphate/sulfate flame retardant. This may be explained by an esterification reaction between boron compounds with the hydroxyl group of cellulose and hemicelluloses, favouring char formation [Uddin 2017; Wang 2004]. Another fire-retardant mechanism of boric acid is due to the development of a glass layer of $B_2O_3$ at the surface when exposed to high temperature, which acts as a protective layer. This layer strongly contributes to reduce the heat released [Mngomezulu 2014].

### 3.2 Characterisation of hemp shiv panels

*Observations*

The visual inspection of the panel produced from treated hemp shiv gave relevant information on its quality and potential performance. The impact of the fire retardant treatment on panel property can be easily observed as illustrated in Fig. 5.

The panels manufactured using hemp shiv treated with 10% and 20% of magnesium sulfate had good cohesion which means that magnesium sulfate did not react chemically with the thermosetting binder or chemically degraded the hemp shiv. Similarly, the cohesion of panels containing boric acid with magnesium sulfate and functionalised silica particles with magnesium sulfate did not seem to be affected by the fire retardant treatments.

The panels manufactured with hemp shiv treated with sulfuric acid, phosphoric acid and ammonium phosphate/sulfate commercial flame retardant were darkened during manufacture. This could be explained by the anticipated thermal degradation highlighted previously by the TGA-TDA analysis. These panels were weaker than the panel made from untreated hemp shiv. The loss of panel integrity could be explained by two phenomena. Firstly, the acid treatments hindered the bio-based binder polymerisation which is usually favoured in alkaline pH range. This assumption was furthermore confirmed as the panel treated with the strong sulfuric acid (sample D), had no integrity as illustrated in Fig. 5. Secondly, the acid treatment could weaken the hemp shiv and therefore reduce the overall integrity of the composite.

An ammonia smell was present from the panel manufactured using the commercial ammonium phosphate/sulfate flame retardant (sample H). Ammonia might have been released by a reaction of the treatment with the bio-based binder which is slightly alkaline, as such pH leads to the transformation of ammonium salt into ammonia.

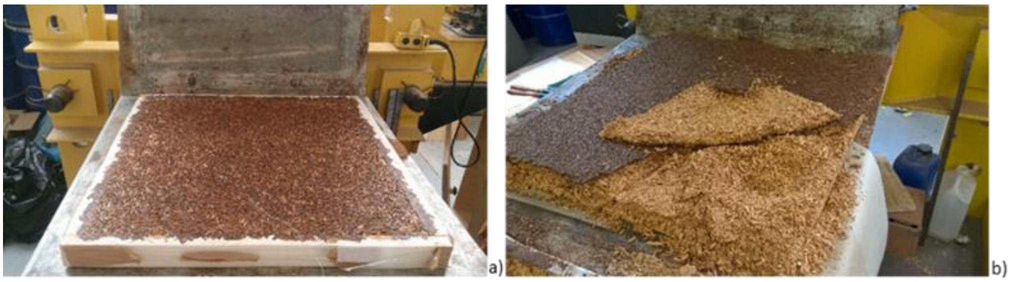

*Fig. 11 : Effect of fire retardant treatment on panel aspect (a. untreated, b. Sulfuric acid treated)*

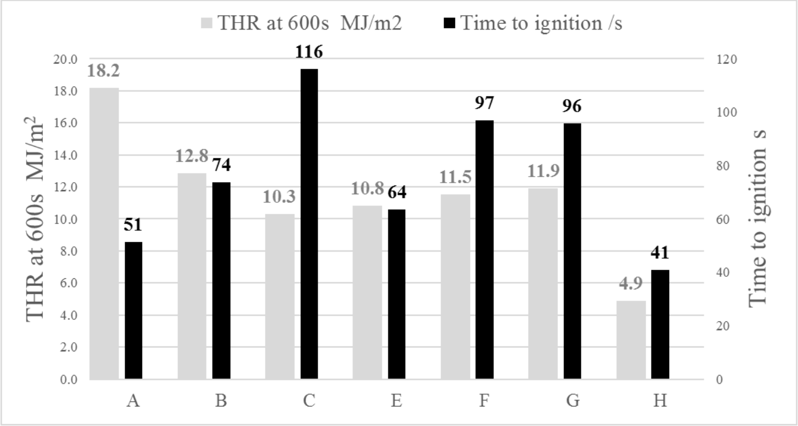

*Fig. 12: Total Heat Released (THR) at 600s and Time to ignition*

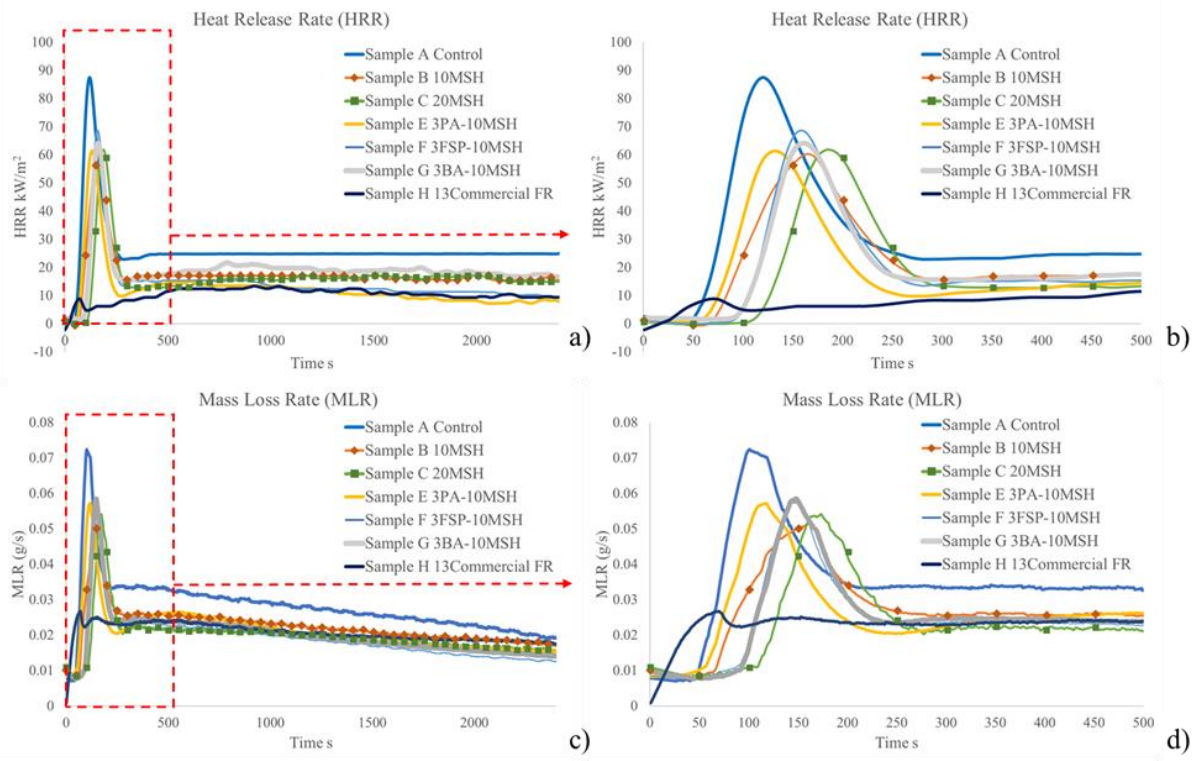

*Fig. 13: Heat Release Rate (HRR) and Mass Loss Rate (MLR) of treated samples*

*C*one calorimeter results

Fig. 7. presents the heat release rate (HRR) and the mass loss rate (MLR) of the treated samples. A clear difference can be observed between the untreated sample A and the treated ones. All treated samples produced similar responses in terms of delayed ignition, lower peak of HRR and MLR, and reduction of pyrolysis compared to sample A. All samples flamed before smouldering became the main type of combustion, apart from the commercial ammonium phosphate/sulfate flame retardant. Indeed, only one sample over the three did flame, whilst the two others only combusted by smouldering. The panel treated with commercial flame retardant presented by far the lowest peaks of HRR and MLR. It can be explained by the TGA/TDA presented earlier: the thermal decomposition was anticipated and the flame-retardant treatment promoted char forming which explains that the heat released was lower when compared to the others samples.

As shown in Fig. 8.a, magnesium sulfate heptahydrate clearly increased the time to ignition. In fact, they were measured at 51 s, 74 s and 116 s for the control sample A, B, and C respectively (Fig. 6). This could be explained by the endothermic decomposition of magnesium sulfate heptahydrate which might have delayed the ignition by cooling effect. Furthermore, the evaporation of water might have diluted the flammable gases which reduced the combustion reaction and heat released. The total heat released by the sample treated with 10% of magnesium sulfate is 12.8 MJ/m$^2$, which is considerably reduced when compared to untreated sample with a THR of 18.2 MJ/m$^2$. However, samples treated with 20% of magnesium sulfate presented a THR of 10.3 MJ/m$^2$, which is not significantly lower than the sample with 10 wt% of magnesium sulfate heptahydrate.

Results obtained for the sample G treated with 3% of boric acid and 10% of magnesium sulfate heptahydrate were similar to those obtained for the sample F treated with 3% functionalised silica particles and 10% magnesium sulfate heptahydrate (Fig. 8.b).

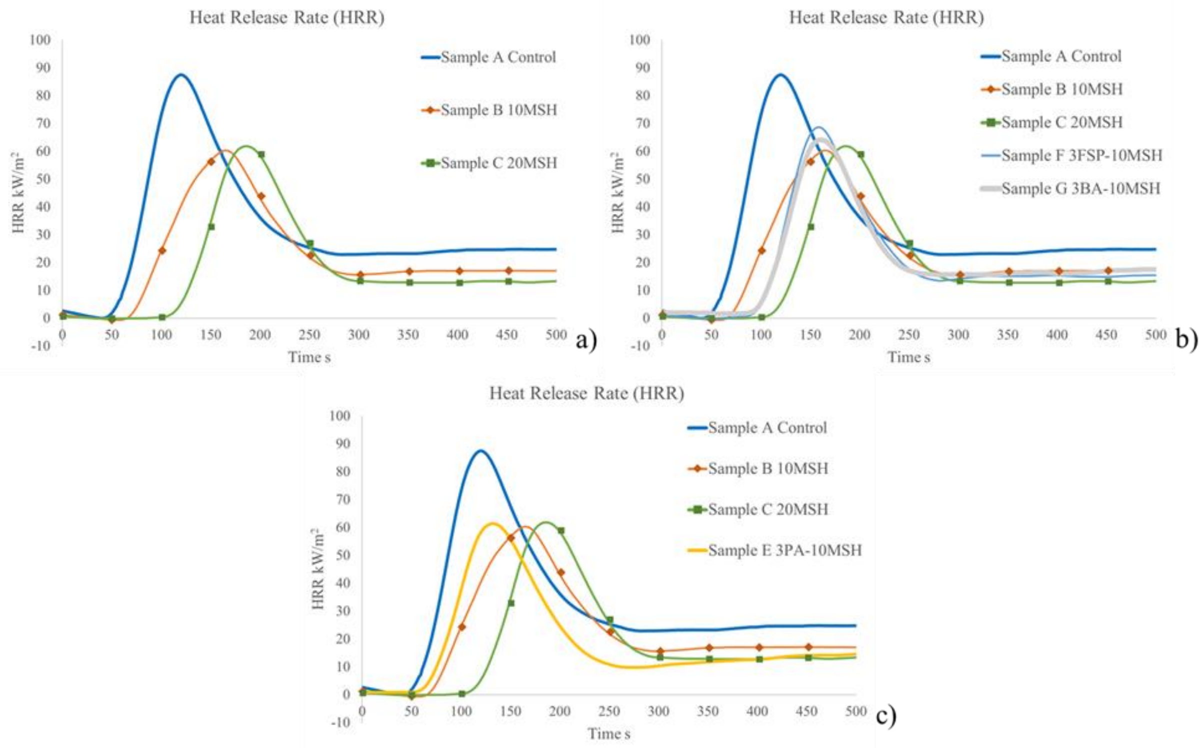

*Fig. 14: Comparison of the HRR between treated samples*

Indeed, time to ignition were respectively 96 s and 97 s and the THR 11.9 MJ/m$^2$ and 11.5 MJ/m$^2$. For both treatments, the time to ignition was increased when compared to samples B. This could be due to the formation of a protective layer at the surface of the sample which acted as a heat shield and thus protected the unexposed material from pyrolysis. These results are very promising for the treatment using functionalised silica particle as it is much less toxic than boric acid for a similar output.

Samples treated with 3% of phosphoric acid and 10% of magnesium sulfate heptahydrate displayed a mean time to ignition of 64 s and a THR of 10.8 MJ/m$^2$. As illustrated in Fig. 8.c, the time to ignition was reduced when compared to the sample B. This could be due to the anticipated decomposition presented in the TGA-TDA analysis. Similarly, to the commercial ammonium phosphate/sulfate flame retardant, the phosphoric acid treatment promotes char forming by cellulose dehydration. Although the decomposition was anticipated by the phosphoric acid, the time to ignition increased with the presence of the magnesium sulfate, which would explain why this parameter was higher for this sample than for the untreated one. The THR was lower than samples treated with boric acid and functionalised silica particles which were respectively of 11.9 MJ/m$^2$ and 11.5 MJ/m$^2$. These results demonstrate how the presence of phosphoric acid combined with magnesium sulfate heptahydrate could improve the fire performance of the hemp shiv panels.

## 4 CONCLUSION

In this study, novel fire retardant formulations were explored to identify potential substitutes to conventional fire retardant additives which are based on ammonium salts or boron compounds. All the treatments reduced the flammability of the hemp shiv insulation panel. However, some treatments affected significantly the hemp shiv panel cohesion. Depending on the additives used, the cohesion could be conserved or drastically reduced. We believe that there was an interaction between the additives and the thermosetting binder which was responsible of the panel strength diminution. This reduction is even more important for strongly acidic treatments.

The magnesium sulfate heptahydrate allowed to improve significantly the flaming behaviour by cooling and gas dilution effects. Advantageously the magnesium sulfate heptahydrate treatment did not seem to affect the hemp shiv panel cohesion. The combination of phosphoric acid with magnesium sulfate heptahydrate showed an improved flame retardancy compared to the panel treated with boric acid combined to magnesium sulfate heptahydrate, and to the panel with magnesium sulfate heptahydrate alone. This behaviour could be explained by the presence of phosphoric acid, which promotes charring. The efficiency of the treatment using sulfuric acid has not been verified because the treated panel lacked cohesion during manufacture. However, TGA-TDA analysis showed similar behaviour to the sample treated with phosphoric acid, which let us believe that it has also a fire retardant effect.

As well as phosphoric acid, the treatment using functionalised silica particles with magnesium sulfate heptahydrate offered better performances than the treatment with boric acid. We believe that the silica particles under thermal exposure formed a shielding layer which protected the non-pyrolysed material from heat.

Several substitutes to boron and ammonium salt compounds using nontoxic and easily accessible flame retardants were found to be effective on hemp shiv panel. It could be interesting to explore the effectiveness of these formulations on other cellulosic materials.

## 5 ACKNOWLEDGEMENTS

ISOBIO project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 636835. The authors acknowledge the help provided by Rory M. Hadden during the cone calorimeter tests at the University of Edinburgh. Thanks to BOIS HD, France for providing access to the hot thermopress.

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