

1  
2 **EFFECT OF BORAX-BORIC ACID AND AMMONIUM**  
3 **POLYPHOSPHATE ON FLAME RETARDANCY OF NATURAL**  
4 **FIBER POLYETHYLENE COMPOSITES**

5 Ritesh Kumar<sup>1,\*</sup>, Jayshree Gunjal<sup>1</sup>, Shakti Chauhan<sup>1,2</sup>

6 <sup>1</sup> Institute of Wood Science and Technology, Bangalore, India.

7 <sup>2</sup> Director, Indian Plywood Industries Research and Training Institute, Bangalore, India.

8 \*Corresponding author: [ritesh@icfre.org](mailto:ritesh@icfre.org); [riteshdavid@gmail.com](mailto:riteshdavid@gmail.com)

9 **Received:** September 16, 2020

10 **Accepted:** April 29, 2022

11 **Posted online:** April 30, 2022

12  
13 **ABSTRACT**

14 Wood fiber filled high density polyethylene composites (WPCs) were prepared using twin  
15 screw extruder and maleated polyethylene as a coupling agent. Bamboo fibers were  
16 initially treated with alkali (NaOH), boric acid - borax (Ba-Bx) and borax (Bx). The treated  
17 and untreated fibers were used in combination with ammonium polyphosphate (APP) to  
18 investigate their synergistic effects on thermal stability, flame retardancy and mechanical  
19 properties. Alkali pretreatment (5 % NaOH) of fibers showed significant improvement in  
20 performance of APP by increasing thermal stability in WPCs. The derivative  
21 thermogravimetric (DTG) results indicate significance of Ba-Bx in promoting char  
22 induction at lower temperatures (340 °C) and thereby, improved the thermal stability in  
23 WPCs. Flammability decreased with addition of flame retardant additives. As compared to  
24 pure WPCs, composites containing APP 10 % / Ba-Bx 5 % exhibited maximum reduction  
25 in average heat release rate (HRR) by 69 %, peak heat release rate (PHRR) by 59 %, total  
26 heat released rate (THR) by 48 % and also increased time to ignition (TTI) by 62 %.  
27 However, no significant difference was found among the combinations i.e., APP with or  
28 without compounds towards reducing the flammability of WPCs. The strength properties  
29 also reduced significantly when boron compounds were added along with APP. In general,  
30 APP alone (15 %) is enough for imparting thermal stability and flame retardancy in WPCs.

31 **Keywords:** Ammonium polyphosphate, boric acid-borax, flammability, fire retardants,  
32 thermal properties, wood polymer composite.

### 33 INTRODUCTION

34 Wood plastic composites (WPCs) have made significant progress in thermoplastic  
35 industries and are finding application in interior automotive panels, garbage pails, crates,  
36 garden equipment, etc. (Hornsby *et al.* 1997). They have also made tremendous progress  
37 in exterior nonstructural or semi-structural building products such as door and window  
38 frames, siding, decking, cladding, floor and roof tiles, fencing, etc. (Schneider *et al.* 2000).  
39 These composites are known to possess excellent durability, dimensional stability, high  
40 rigidity, and relatively low density (Schneider *et al.* 2000, Ashori 2008). However, the  
41 potential use of WPCs is greatly restricted by their poor fire resistance property (Mouritz  
42 and Gibson 2006, Chapple and Anandjiwala 2010, Salemane and Luyt 2006). During a fire  
43 situation, the polymer burns and drips, leading to hazardous fire situations (Kozłowski and  
44 Władysław-Przbylak 2008, Panagiotou and Levendis 1994). PVC is a self-extinguishing  
45 material, but they generate toxic gases while burning and create serious risk to life  
46 (Panagiotou and Levendis 1994). Therefore, from the point of view of fire safety, the users  
47 are insisting on fire resistant materials.

48 In order to impart flame retardancy in WPCs, many fire retardants (FR) chemicals have  
49 been introduced. Antimony based systems along with halogen compounds provide good  
50 flame retardancy, but their large-scale industrial use is restricted because of environmental  
51 issues (Kozłowski *et al.* 1999, Chen *et al.* 2006). Certain nano particles like nano clay,  
52 carbon tube, nano-SiO<sub>2</sub>, TiO<sub>2</sub> and ZnO are used as FR additives for imparting flame  
53 retardancy in WPCs (Pan *et al.* 2014, Devi *et al.* 2013, Palza *et al.* 2010). However, the  
54 high price of nano additives makes their use unaffordable in commodity products such as  
55 the construction sector. Boron compounds have long been used as FR additives for wood  
56 and WPCs (Chen *et al.* 2006, Pan *et al.* 2014). Effectiveness of borax and boric acid has

57 been widely reported (LeVan 1984, Nagieb *et al.* 2011). Borax reduces flame spread, but  
58 it promotes glowing, whereas, boric acid subdues glowing but has minimum effect on flame  
59 spread. Therefore, borax and boric acid are generally used together (Wang *et al.* 2004).  
60 Further, phosphorus-based FR (phosphoric acid) and their salts such as monoammonium  
61 phosphate and diammonium phosphate are the oldest and most commonly used FRs.  
62 Ammonium polyphosphate (APP) is considered as one of the most effective FR additives  
63 for WPCs. However, to achieve required flame retardancy, higher loading of APP is  
64 suggested, which increases cost and reduces material properties.

65 Although the effect of APP and boron-based FR on properties of WPCs has been studied  
66 extensively, studies on synergistic effect of APP and boric acid-borax (Ba-Bx) on FR  
67 properties of polymer are meager (Kurt *et al.* 2012). Kurt *et al.* (2012) have investigated  
68 the utilization of boron compounds (BCs) as synergists with APP in WPCs manufacturing,  
69 however, the method adopted in present study is different in terms of pretreating the  
70 bamboo fibers with BCs and using these fibers in combination with ammonium  
71 polyphosphate (APP) for investigating their combined effects on thermal stability, flame  
72 retardancy and mechanical properties of WPCs. Moreover, the effect of alkali (NaOH)  
73 pretreatment of fibers on performance of FR additives i.e., APP and BCs has not been  
74 studied. The objective of this study is to examine the feasibility of imparting flame-  
75 retarding functions to WPCs through alkali washing of wood fibers prior to their  
76 pretreatment with BCs i.e., boric acid - borax (Ba-Bx) and borax (Bx) and use these  
77 pretreated fibers along with APP as FRs. The aim of this work is to develop economically  
78 competitive WPCs with better flame retardancy.

79

## 80 MATERIALS AND METHODS

### 81 *Materials*

82 Reliance make high-density polyethylene (HD50MA180) was used in this study. Polymer  
83 density is around 0,950 g/cm<sup>3</sup> and melt flow index is 20 g /10 min (190 °C / 2,16 kg). APP  
84 (phase II, degree of polymerization >1000) was procured from Advance Inorganics, New  
85 Delhi. The coupling agent (CA) maleic anhydride grafted polyethylene M603 having melt  
86 flow index of 25 g/10 min was supplied by Dupont, India. Boric acid (Ba) and Borax (Bx)  
87 were used as boron compounds (BCs). Boric acid, borax, and sodium hydroxide were  
88 obtained from M/s Himedia. All the chemicals used for experiments were analytical  
89 reagent grade and were used without further purification. Freshly harvested wood biomass  
90 was processed to pass – 60+80 mesh sieve. Oven dried wood fibers were used for  
91 experiments.

### 92 *Processing*

93 A part of oven dried wood fibers was chemically treated with sodium hydroxide (5 % w/w)  
94 for 4 hrs for surface activation and removal of impurities from the cellulose fibre and for  
95 increasing adhesion and compatibility of fibers to polymer matrix (Islam *et al.* 2012; Lee  
96 *et al.* 2009). The alkali treated fibers were washed with hot distilled water (four times) and  
97 oven-dried to constant weight at 80 °C. One unit of Bx was mixed with one unit of Ba and  
98 dissolved in warm water. A part of wood fiber was soaked in 5 % aqueous solution of Ba-  
99 Bx (Jiang *et al.* 2011). The treated wood fibers were air dried for four days followed by  
100 oven drying to constant weight at 80 °C. Oven dried HDPE, APP, CA, and wood fibers  
101 were used for further processing. The components were pre-mixed in a double-cone  
102 blender and then extruded using a twin-screw extruder. The screw speed of 150 rpm and  
103 temperature profile of 140 °C to 160 °C in the barrel and 180 °C near nozzle was

104 maintained. The extruded composite granules were injection moulded into test specimens  
 105 using a closed loop 60 tonnes injection moulding machine (L & J make). The injection  
 106 molding process parameters were 180 °C to 190 °C temperature and injection pressure of  
 107 100 bars. Compositions of wood fiber composites (WPCs) with and without flame retardant  
 108 additives are summarized in Table 1.

109 **Table 1:** Experimental formulations studied (weight in grams).

Sample	Polymer	Fiber	CA	AO	Wax		APP	FT	Ba-Bx
Control	575	400	25	10	10		-	-	-
IFR-1	575	400	25	10	10		50	-	-
IFR-2	575	400	25	10	10		100	-	-
IFR-3	575	400	25	10	10		150	-	-
IFR-4	575	400	25	10	10		100	√	×
IFR-5	575	400	25	10	10		100	×	√
IFR-6	575	400	25	10	10		100	√	√
IFR-7	575	400	25	10	10		100	√	Bx
CA-Coupling agent; AO- Anti oxidant; APP-Ammonium polyphosphate; FT- Fiber treated with NaOH; Ba-Bx-Boric acid Borax; Bx-Borax									

110

111

## 112 **Testing**

113 Flexural and tensile tests were conducted as per ASTM D790 (ASTM 2014) and ASTM  
 114 D638 (ASTM 2015), respectively, using Shimadzu make model AGIS10, 10 kN universal  
 115 testing machine. For tensile test, dumbbell shaped specimens were used (Type I) with span  
 116 length of 100 mm. Crosshead speed was 5 mm/min. Flexural strength was determined using  
 117 standard specimens (127 mm x 13,2 mm x 6,2 mm) and crosshead speed of 2,8 mm / min.  
 118 Five replicates were evaluated for each treatment group. The thermal degradation  
 119 properties were studied under nitrogen atmosphere. Thermo-gravimetric analysis (TGA)  
 120 was carried out using TGA Q500 V20.2 Build 27. A known quantity of sample was placed

121 in a platinum crucible and heated from ambient to 800 °C at heating rate of 10 °C min<sup>-1</sup>  
122 and 60 ml·min<sup>-1</sup> air flow rate. Three replicates were evaluated for each treatment group.  
123 The thermal degradation profiles of the samples were derived by applying the derivative  
124 thermogravimetry technique (Haykira-Acma 2003). The flammability properties of WPCs  
125 were measured using cone calorimeter at CIPET, LARPM Bhubaneswar. The compounded  
126 specimens were compression moulded into standard size specimens (100 mm x 100 mm x  
127 4 mm) for cone calorimeter test. Heat release rate was determined as per ISO 5660 (ISO  
128 2015). An external heat flux of 50 kW / m<sup>2</sup> was applied. The flammability was also  
129 performed with limited oxygen index (LOI) as per ASTM D 2863 (ASTM 2019) and two  
130 replicates were evaluated for each treatment group. The data analysis was performed using  
131 SPSS statistical software. One way ANOVA was performed to understand statistically  
132 significant differences in each treatment group.

133

## 134 **RESULTS AND DISCUSSION**

### 135 *Mechanical performance*

136 The effect of FRs on strength properties of WPCs has been evaluated. The results are  
137 presented in Table 2. In case of WPC prepared with untreated fibers (pure WPC, IFR 1,  
138 IFR2 and IFR3) addition of APP had insignificant influence on flexural modulus or  
139 strength but tensile strength at 150 g of APP (IFR3) exhibited significant decline from 32  
140 MPa to 26 MPa. This suggests that higher loading of APP has affected interfacial adhesion  
141 between fiber and polymer matrix. When treated fibers were used for making WPC along  
142 with APP, a marginal increase in flexural strength (FS) was observed which was  
143 statistically higher than with untreated fibers (IFR2 v/s IFR4). This shows the influence of

144 alkali washing of fibers on FS of WPCs, added with APP. Ikhlef *et al.* (2012) studied the  
 145 effect of alkali washing and reported improvement in strength properties of composite due  
 146 to improved interfacial adhesion between matrix and cellulosic fiber. The addition of boron  
 147 compound in the formulation resulted in significant loss in strength (both tensile and  
 148 flexural) and flexural modulus of APP incorporated composites irrespective of fiber  
 149 treatment. FS and FM of IFR1, IFR2, IFR3 and IFR4 samples doesn't change significantly.  
 150 This shows that addition of APP alone (up to 15 %) doesn't reduce FS and FM of WPCs.  
 151 However, significant reduction in FS (10 % to 14 %) and FM (6 % to 18 %) is seen in  
 152 IFR5, IFR6 and IFR7 combinations where, BCs was added along with APP. Similarly, TS  
 153 values are also found to be minimum in groups which has BCs in their compositions (IFR5,  
 154 IFR6 and IFR7).

155 **Table 2:** Tensile and flexural properties of WPC treated with fire retardants (Values are  
 156 mean  $\pm$  standard deviation of minimum triplicate determination. Values in column with  
 157 different lowercase superscript letter are statistically significant ( $p < 0.05$ )).

Samples	Flexural Modulus (MPa)	Flexural Strength (MPa)	Maximum displacement (mm)	Tensile Strength (MPa)
Pure WPC	2520 ( $\pm$ 52) <sup>c</sup>	37 ( $\pm$ 1,0) <sup>bcd</sup>	3,3 ( $\pm$ 0,3) <sup>b</sup>	32 ( $\pm$ 0,4) <sup>d</sup>
IFR-1	2522 ( $\pm$ 62) <sup>c</sup>	38 ( $\pm$ 0,6) <sup>d</sup>	2,9 ( $\pm$ 0,3) <sup>ab</sup>	31 ( $\pm$ 0,1) <sup>cd</sup>
IFR-2	2408 ( $\pm$ 130) <sup>bc</sup>	36 ( $\pm$ 0,9) <sup>b</sup>	2,8 ( $\pm$ 0,1) <sup>a</sup>	31 ( $\pm$ 0,2) <sup>cd</sup>
IFR-3	2552 ( $\pm$ 53) <sup>c</sup>	36 ( $\pm$ 0,4) <sup>bc</sup>	2,8 ( $\pm$ 0,1) <sup>a</sup>	26 ( $\pm$ 0,8) <sup>b</sup>
IFR-4	2510 ( $\pm$ 13) <sup>c</sup>	38 ( $\pm$ 0,3) <sup>cd</sup>	3,0 ( $\pm$ 0,1) <sup>ab</sup>	30 ( $\pm$ 0,4) <sup>c</sup>
IFR-5	2244 ( $\pm$ 99) <sup>ab</sup>	33 ( $\pm$ 0,5) <sup>a</sup>	2,6 ( $\pm$ 0,05) <sup>a</sup>	26 ( $\pm$ 0,3) <sup>b</sup>
IFR-6	2393 ( $\pm$ 4) <sup>bc</sup>	33 ( $\pm$ 0,1) <sup>a</sup>	2,7 ( $\pm$ 0,05) <sup>a</sup>	23 ( $\pm$ 2,0) <sup>a</sup>
IFR-7	2172 ( $\pm$ 10) <sup>a</sup>	32 ( $\pm$ 0,4) <sup>a</sup>	2,9 ( $\pm$ 0,2) <sup>ab</sup>	23 ( $\pm$ 0,1) <sup>a</sup>

158

159 Wang *et al.* (1996) studied interaction of boric acid with polymer constituents of a  
160 wood/polystyrene composite material and reported that boric acid gets chemically bonded  
161 with wood components during manufacturing of composite materials. This may alter the  
162 efficiency of coupling agent in improving the compatibility of fiber with the polymer.  
163 Addition of APP in small quantity (up to 10 %) is not influencing tensile or flexural  
164 properties but higher loading (15 %) was indicating adverse impact. Kurt *et al.* 2012, found  
165 that 25% APP loading resulted in a very sharp decrease in TS value (49.04%) of WPCs,  
166 however, TS decreased between 18 % to 27 % in groups where BCs was added along with  
167 APP.

#### 168 ***Thermal degradation under inert atmosphere***

169 The results on thermal degradation of WPCs under inert atmosphere are summarized in  
170 Table 3. The pyrolysis of biomass can be divided into three different zones i.e., moisture  
171 evaporation, initial devolatilisation and major devolatilisation zone (Kumar and  
172 Chandrashekar 2014). Fig. 1 shows that DTG curve of wood fibers, WPCs and APP. The  
173 initial weight loss, between 40 °C to 100 °C is mainly due to removal of moisture and lighter  
174 volatiles. After moisture evaporation, weight loss resulting at 150 °C to 350 °C is attributed  
175 to thermochemical decomposition and subsequent de-volatilization of samples (Haykira-  
176 Acma 2003; Kumar *et al.* 2021). The pure APP showed one sharp decomposition peak  
177 ( $T_{peak1}$ ) at 200 °C with initial devolatilisation temperature at 110 °C. During initial thermal  
178 degradation, mainly ammonia and moisture escapes as volatiles from APP. The major  
179 decomposition temperature of APP ranges from 550 °C to 650 °C, with  $T_{peak2}$  of 648 °C,  
180 which is mainly due to the generation of highly cross-linked pyro/polyphosphoric acid  
181 (Stark *et al.* 2010). The residue char in pure APP at 500 °C and 700 °C was around 63 %  
182 and 19 %, respectively. Fig. 2 shows the DTG curve of WPCs with and without APP. A



183 clear shift in major devolatilisation temperature towards higher side is observed by  
 184 increasing the amount of APP in WPCs Fig. 2. For pure WPC, major devolatilization  
 185 temperature ( $T_{MD}$ ) ranged from 350 °C to 480 °C.  $T_{MD}$  shifted to higher temperature range  
 186 (385 °C to 520 °C) with addition of APP. The shift in  $T_{MD}$  to higher temperature range  
 187 indicates towards thermal stability provided by APP (Table 3). Among IFR1, IFR2 and  
 188 IFR3 samples, highest  $T_{MD}$  was observed in IFR3 samples. For IFR3,  $T_{MD}$  ranged from 420  
 189 °C to 520 °C, with  $T_{peak2}$  of 488 °C. The initial devolatilisation temperature ( $T_{ID}$ ) ranged from  
 190 190 °C to 320 °C in IFR1, IFR2, IFR3 and IFR4 samples.  $T_{ID}$  shifted towards higher  
 191 temperature (200 °C to 340 °C) when BCs are added with APP as FRs (IFR5, IFR6 and  
 192 IFR7) Table 3.

193 **Table 3:** TGA under pyrolysis ( $N_2$ ) conditions.

Sample	Initial devolatilisation temperature range (°C)	$T_{Peak1}$ (°C)	Char devolatilisation temperature range (°C)	$T_{peak2}$ (°C)	Maximum rate of weight loss at peak temperature (mg/min)	Residue (%) at 500 °C	Residue (%) at 700 °C
Biomass	210-330	300	360-470	410	0,205	2,0	1,2
Pure WPCs	200-350	330	350-480	474	1,772	12,3	1,4
IFR-1	190-320	290	385-500	471	2,047	18,4	5,7
IFR-2	190-320	290	385-500	479	1,650	20,7	7,3
IFR-3	190-320	300	420-520	488	1,094	23,3	12,5
IFR-4	190-320	280	380-500	473	0,857	20,7	8,0
IFR-5	200-330	300	340-510	484	1,043	24,1	10,5
IFR-6	200-330	310	340-510	467	0,922	22,6	9,5
IFR-7	200-340	330	340-510	481	1,156	18,1	7,7
IFR-8*	110-220	190	550-660	648	2,052	62,7	19,5

\* IFR-8- Pure APP

194 For IFR3, char residue at 500 °C and 700 °C was 23 % and 13 %, respectively. Fig. 3 shows  
 195 the DTG curve of neat WPC, IFR2 and IFR4 samples. Among these combinations,  
 196 maximum weight loss at peak temperatures ( $T_{peak2}$ ) was 1,8 mg/min, 1,7 mg/min and 0,9  
 197

198 mg/min in pure WPC, IFR2 and IFR4, respectively (Table 3). The rate of weight loss  
199 indicates the reactivity of the samples. IFR4 showed lowest rate of thermal degradation  
200 i.e., 0,9 mg/min (Table 3). Fig. 4 shows DTG curve of neat WPC, IFR4 and IFR6 samples.  
201  $T_{MD}$  ranged from 380 °C to 500 °C in IFR4, whereas, it ranged from 340 °C to 510 °C in  
202 IFR6 (Table 3). This shift in  $T_{MD}$  towards lower side (340 °C) in IFR6 sample can be  
203 attributed to early charring in WPC, caused by boric acid. Wang *et al.* 2004 concluded that  
204 boric acid catalyzes the dehydration and other oxygen-eliminating reactions of wood at a  
205 relatively low temperature (approximately 100 °C – 300°C) by catalyzing the isomerization  
206 of the newly formed polymeric materials and by forming aromatic structures, which  
207 contributes partly to the effects of boric acid on promoting the charring and fire retardation  
208 of wood. Fig. 4. confirms the significance of boric acid in promoting char formation at  
209 lower temperatures. Fig.5 shows DTG curve of WPC, IFR6 and IFR7 samples. Among  
210 IFR6 and IFR7 samples, rate of weight loss at  $T_{peak2}$  was found to be minimum (0,74  
211 mg/min) in IFR6 samples. Further, the char residues in IFR6 and IFR7 at 500 °C was 23 %  
212 and 18 %, respectively. This shows that char residue with higher thermal stability is formed  
213 with Ba-Bx/APP, as compared to borax with APP. The overall result shows the usefulness  
214 of alkali washing of fibers and use of BCs as synergist in combination with APP for  
215 obtaining improved thermal stability in WPCs.

216

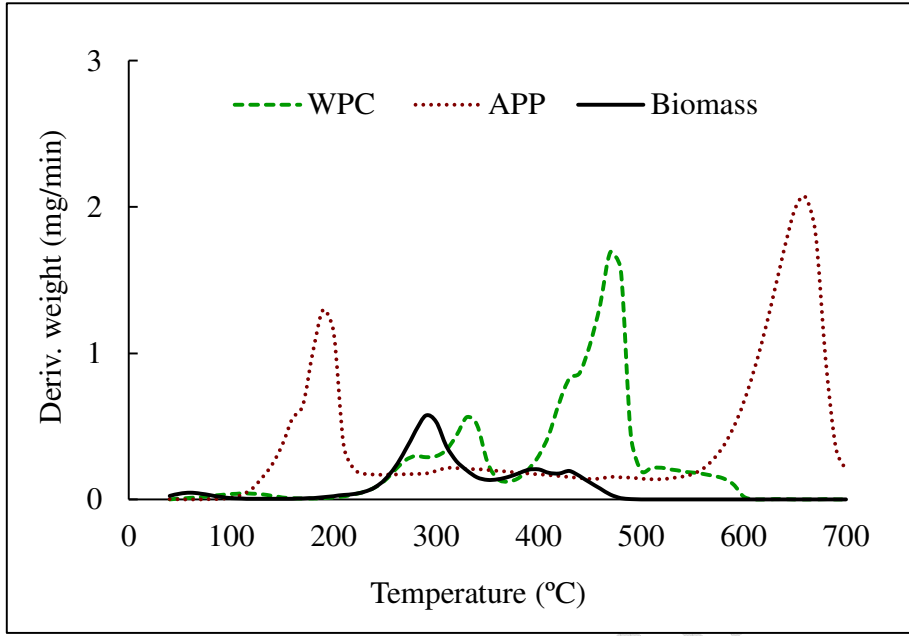
217

218

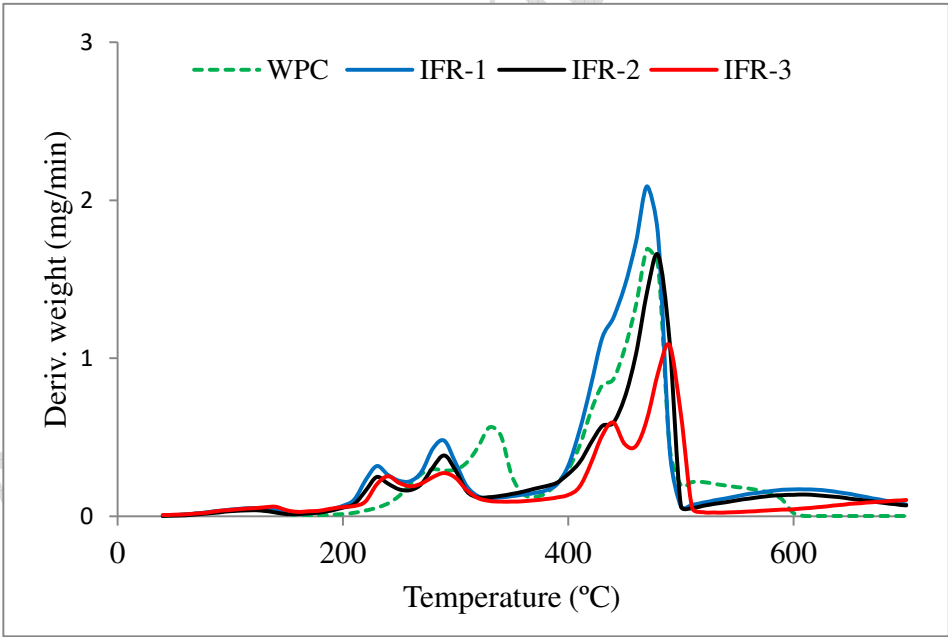
219

220

221  
222  
223  
224  
225  
226  
227  
228  
229  
230  
231  
232  
233  
234  
235  
236  
237  
238  
239  
240  
241  
242  
243  
244  
245  
246

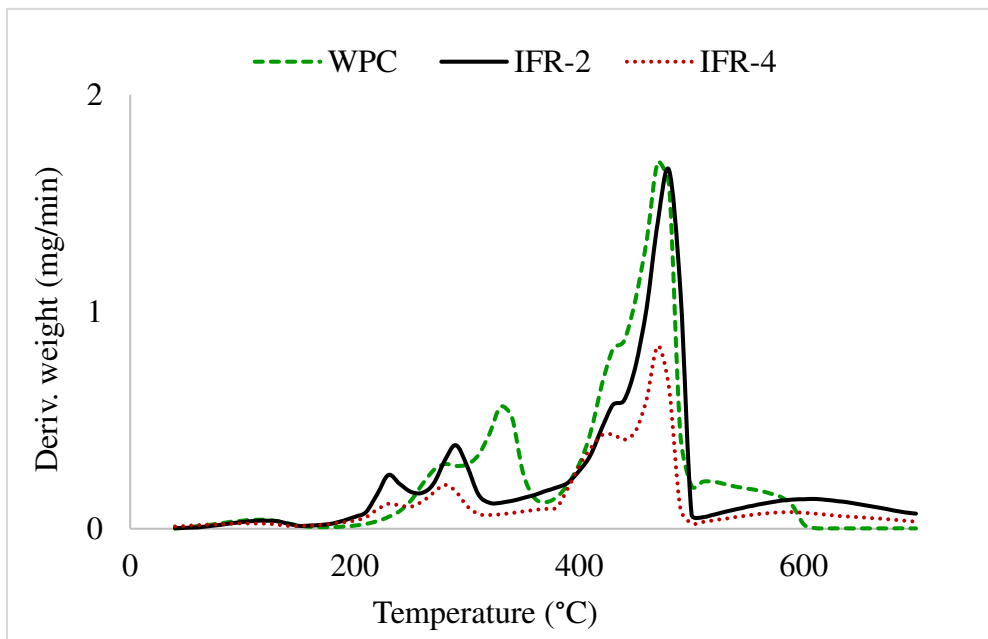


**Figure 1:** DTG curve of WPC, APP and Bamboo fibers.

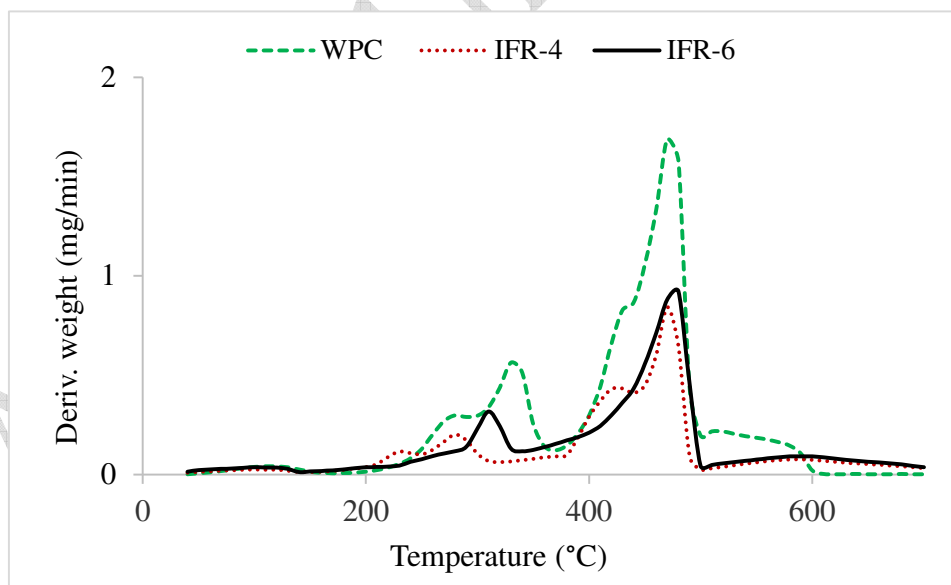


**Figure 2:** DTG curve of WPC, IFR1 (APP 5 %), IFR2 (APP 10 %) and IFR3 (APP 15 %) samples.

247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267  
268  
269  
270  
271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292

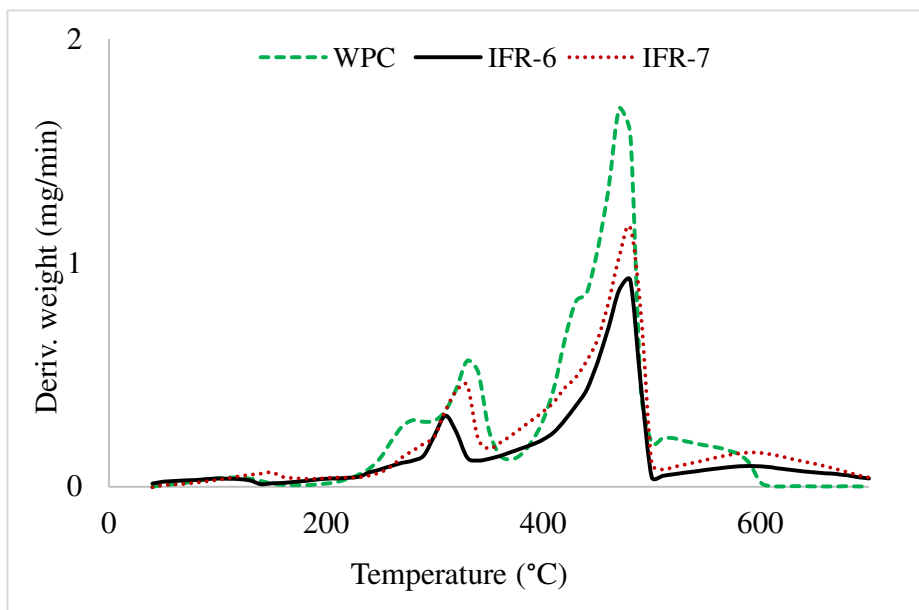


**Figure 3:** DTG curve of WPC, IFR2 (APP 10 %) and IFR4 (APP 10 %+ Fibers treated with NaOH).



**Figure 4:** DTG curve of WPC, IFR4 (APP 10 % + NaOH treatment) and IFR6 (NaOH treatment + APP 10 % + Ba-Bx).

293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322  
323  
324  
325  
326  
327  
328



**Figure 5:** DTG curve of WPC, IFR6 (NaOH treatment + APP 10 % + Ba-Bx) and IFR7 (NaOH treatment + APP 10 % + Bx).

***Flammability properties***

The flammability properties of WPCs (with and without flame additives) were determined by cone calorimeter and LOI tests. The results on average heat release rate (HRR), the peak HRR, total heat release rate (THR), time to ignition (TTI), time to flame out (TTF), mass loss rate (MLR) and limited oxygen index (LOI) are summarized in Table 4.

329 **Table 4:** Cone calorimeter and LOI results of WPCs with and without flame additives  
 330 (Value in parenthesis is standard deviation. Values in column with different lowercase  
 331 superscript letter are statistically significant ( $p < 0,05$ )).

Sample code	Average HRR (kW/m <sup>2</sup> )	Peak HRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	TTI (s)	TTF (s)	MLR (g/s)	LOI (%)
WPC	196 (±25) <sup>c</sup>	457 (±37) <sup>d</sup>	64 (± 2) <sup>d</sup>	13 (±4) NS	297 (±20) <sup>a</sup>	19 (±3) <sup>e</sup>	16,1 (±0,1) <sup>a</sup>
IFR-1	125 (±11) <sup>b</sup>	370 (±23) <sup>c</sup>	57 (± 2) <sup>cd</sup>	12 (±7) NS	320 (±46) <sup>a</sup>	15 (±1) <sup>cd</sup>	16,8 (±0,2) <sup>b</sup>
IFR-2	110 (±7) <sup>b</sup>	353 (±15) <sup>c</sup>	56 (± 2) <sup>c</sup>	13 (±1) NS	347 (±34) <sup>ab</sup>	13 (±1) <sup>bc</sup>	16,9 (±0,1) <sup>b</sup>
IFR-3	80 (±7) <sup>a</sup>	235 (±7) <sup>b</sup>	52 (± 6) <sup>c</sup>	20 (±1) NS	453 (±40) <sup>c</sup>	08 (±1) <sup>a</sup>	19,2 (±0,1) <sup>c</sup>
IFR-4	64 (±1) <sup>a</sup>	196 (±26) <sup>ab</sup>	42 (± 3) <sup>b</sup>	16 (±1) NS	457 (±71) <sup>c</sup>	12 (±0,7) <sup>abc</sup>	17,9 (±0,1) <sup>d</sup>
IFR-5	64 (±1) <sup>a</sup>	186 (±0,6) <sup>ab</sup>	44 (± 3) <sup>b</sup>	20 (±1) NS	401 (±23) <sup>bc</sup>	10 (±1) <sup>ab</sup>	17,7 (±0,1) <sup>d</sup>
IFR-6	60 (±3) <sup>a</sup>	186 (±4) <sup>ab</sup>	33 (± 0,3) <sup>a</sup>	21 (±3) NS	332 (±9) <sup>ab</sup>	18 (±0,3) <sup>de</sup>	17,3 (±0,1) <sup>c</sup>
IFR-7	59 (±1) <sup>a</sup>	179 (±0,4) <sup>ab</sup>	32 (± 0,5) <sup>a</sup>	18 (±3) NS	300 (±6) <sup>ab</sup>	20 (±0,1) <sup>e</sup>	16,2 (±0,1) <sup>a</sup>

NS: Not significant  
 THR (MJ/m<sup>2</sup>): Total heat release  
 TTI (s): Time to ignition  
 TTF (s): Time to flame out  
 MLR (1000 mg/s): Mass loss rate

332  
 333 The best result on LOI was seen with IFR3 (Table 4). Compared to pure WPCs, LOI was  
 334 increased by 19 % in IFR3. All FRs showed positive influence on flame properties of WPCs.  
 335 Peak HRR decreased from 457 kW/m<sup>2</sup> to 179 kW/m<sup>2</sup>, which is approximately 61 % lower than  
 336 pure WPCs. Average HRR and peak HRR (kW/m<sup>2</sup>) in IFR2 and IFR4 combinations decreased  
 337 from 110 and 353 to 64 and 196, respectively. Compared to pure WPC, higher reduction in  
 338 HRR was seen in IFR4 (67 %) than IFR2 (44 %). This shows alkali washing enhances  
 339 performance of APP decreasing HRR in WPCs. The order of decrease in average HRR  
 340 (kW/m<sup>2</sup>) is as follows; Pure WPC = 196 > IFR1 = 125 > IFR2 = 110 > IFR3 = 80 > IFR4 and  
 341 IFR5 = 65 > IFR6 = 60 > IFR7 = 59 (Table 4). Through IFR6 and IFR7 combinations,  
 342 maximum reduction in average heat release rate (HRR) was by 69 %, peak heat release rate  
 343 (PHRR) by 59 %, total heat released rate (THR) by 48 % and time to ignition (TTI) was  
 344 increased by 62 % as compared to pure WPCs. However, the statistical analysis indicated no

345 significant difference among different combinations (IFR3, IFR4, IFR5, IFR6 and IFR7)  
346 towards reducing HRR in WPCs (Table 4). This shows that APP (15 %) is equally effective in  
347 reducing HRR as it is with combination of BCs along with APP. THR ( $\text{MJ}/\text{m}^2$ ) reduced  
348 significantly with addition of FRs (Table 4). The result indicated significant increase in TTF  
349 in IFR3 and IFR4 samples (Table 4). This shows that 15% APP is appropriate amount for  
350 achieving effective flame retardancy in WPCs. THR decreased from  $64 \text{ MJ}/\text{m}^2$  to  $32 \text{ MJ}/\text{m}^2$  in  
351 IFR7, which is approximately 50 % lower than pure WPC. Wang *et al.* 2004 found that during  
352 combustion, borates form an impenetrable glass coating on a materials surface and restricts the  
353 supply of oxygen which prevents further propagation of flame from one part to another. The  
354 FRs combination showed no significant difference in prolonging the TTI during fire (Table 4).  
355 The most delayed ignition was in IFR6, where TTI is prolonged by 62 %, as compared to pure  
356 WPC. The same may be attributed to the positive impact of Ba-Bx which promotes early char  
357 formation in samples during fire. During combustion, borax suppresses flame spread but  
358 promotes glowing. Boric acid, on the other hand, increases the rate of depolymerization of  
359 cellulosic fibers and enables char production at considerably lower temperature ( $120 \text{ }^\circ\text{C}$  to  $180$   
360  $^\circ\text{C}$ ) and suppresses glowing (Shafizadeh 1984). It also prevents the flame spread to some extent  
361 by releasing water (Shafizadeh 1984). Table 4 shows average MLR of WPCs with and without  
362 the flame additives. It is evident that the incorporation of FRs decreases the MLR of WPCs  
363 during combustion. For IFR3, the average MLR decreased most from  $19 \text{ g}/\text{s}$  to  $8 \text{ g}/\text{s}$ , which is  
364 approximately 58 % lower than that of neat WPC (Table 4). This shows that APP (15 %) is  
365 most effective in reducing average MLR in WPCs.

366

367

368

## CONCLUSIONS

369 Effect of BCs and APP on flame retardancy, thermal stability and mechanical properties in  
370 WPCs have been investigated. Prior to its pretreatment with BCs, wood fibers were washed  
371 with NaOH. Alkali washing of wood fibers showed positive influence on flexural strength,  
372 thermal stability and HRR of WPCs. The addition of BCs with APP, initiated early char  
373 formation in WPC. Best results on thermal stability in WPC were obtained under condition  
374 i.e., NaOH 5 % / Ba-Bx 5% / APP 10 %. Second best result was with addition of 15 % APP  
375 alone, wherein, major devolatilization temperature shifted to higher temperature range i.e., 385  
376 °C - 520 °C. The combination i.e., alkali washing of fibers/BCs/APP also showed better flame  
377 retardancy in WPCs, leading to improvement in peak HRR, THR and TTI. However, the best  
378 results on MLR, TTF and LOI was obtained by using APP (15 %) as FR. Keeping in view the  
379 above results on thermal stability and flame retardancy, the appropriate combination  
380 recommended for further research is NaOH 5 % / Ba-Bx 5% / APP 15 %. The strength  
381 properties of WPCs reduced significantly on adding BCs in the composition. In general, the  
382 effect of combination of Ba-Bx and APP leads to better thermal stability and flame retardancy  
383 in WPCs.

## 384 REFERENCES:

385 **ASTM 2019.** D2863-19: Standard Test Method for Measuring the Minimum Oxygen  
386 Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index). ASTM  
387 International, West Conshohocken, PA, USA. [http://www.astm.org/cgi-](http://www.astm.org/cgi-bin/resolver.cgi?D2863)  
388 [bin/resolver.cgi?D2863](http://www.astm.org/cgi-bin/resolver.cgi?D2863)

389 **ASTM 2014.** D638-14: Standard Test Method for Tensile Properties of Plastics. ASTM  
390 International: West Conshohocken, PA, USA. <https://doi.org/10.1520/D0638-14>



391 **ASTM 2015.** D790-15: Standard test methods for flexural properties of unreinforced and  
392 reinforced plastics and electrical insulating materials. ASTM International: West  
393 Conshohocken, PA, USA. <https://doi.org/10.1520/D0790-15>

394 **Ashori, A. 2008.** Wood-plastic composites as promising green-composites for automotive  
395 industries. *Bioresour Technol* 99(11): 4661-4667.  
396 <https://doi.org/10.1016/j.biortech.2007.09.043>

397 **Chapple, S.; Anandjiwala, R. 2010.** Flammability of Natural Fiber-reinforced Composites  
398 and Strategies for Fire Retardancy: A Review. *J Thermoplast Compos Mater* 23(6): 871–893.  
399 <https://doi.org/10.1177/0892705709356338>

400 **Chen, X.L.; Yu, J.; Guo, S.Y. 2006.** Structure and properties of polypropylene composites  
401 filled with magnesium hydroxide. *J Appl Polym Sci* 102(5): 4943-4951.  
402 <https://doi.org/10.1002/app.24938>

403 **Devi, R.R.; Gogoi, K.; Kowar, B.K.; Maji, T.K. 2013.** Synergistic effect of nanoTiO<sub>2</sub> and  
404 nanoclay on mechanical properties, flame retardancy, UV stability, and antibacterial  
405 properties of wood polymer composites. *Polym Bull* 70(4): 1397-1413.  
406 <https://doi.org/10.1007/s00289-013-0928-x>

407 **Haykira-Acma, H. 2003.** Combustion characteristic of different biomass materials. *Energy*  
408 *convers Manag* 44(1): 155-162 [https://doi.org/10.1016/S0196-8904\(01\)00200-X](https://doi.org/10.1016/S0196-8904(01)00200-X)

409 **Hornsby, P.R.; Hinrichsen, E.; Tarverdi, K. 1997.** Preparation and properties of  
410 polyethylene composites reinforced with wheat and flax straw fibre: Part II Analysis of

411 composite microstructure and mechanical properties. *J Mat Sci* 32(4): 1009–1015.  
412 <https://doi.org/10.1023/A:1018578322498>

413 **Ikhlef, S.; Nekkaa, S.; Guessoum, M.; Haddaoui, N. 2012.** Effects of Alkaline Treatment  
414 on the Mechanical and Rheological Properties of Low-Density Polyethylene/*Spartium*  
415 *junceum* Flour Composites. *Inter Scholar Res Notices* Article ID 965101: 7p.  
416 <https://doi.org/10.5402/2012/965101>

417 **Islam, Md. S.; Hamdan, S.; Jusoh, I.; Rehman, Md. R.; Ahmed, A.S. 2012.** The effect of  
418 alkali pretreatment on mechanical and morphological properties of tropical wood polymer  
419 composites. *Mater Des* 33: 419-424. <https://doi.org/10.1016/j.matdes.2011.04.044>

420 **ISO 2015.** 5660-1: Reaction to fire tests-Heat release, smoke production and mass loss rate,  
421 Part 1: Heat release rate (cone calorimeter method). ISO International.  
422 <https://www.iso.org/obp/ui/#iso:std:iso:5660:-1:ed-3:v1:en>

423 **Jiang, J.; Yang, Y.; Li, J. 2011.** Effect of three boron flame retardants on thermal curing  
424 behavior of urea formaldehyde resin. *J Therm Anal Calorim* 105(1): 223-228.  
425 <https://doi.org/10.1007/s10973-011-1307-1>

426 **Kozłowski, R.; Wesolek, D.; Władysław-Przybylak, M. 1999.** Combustibility and toxicity of  
427 board materials used for interior fittings and decorations. *Polym Degrad Stab* 64(3): 595-600.  
428 [https://doi.org/10.1016/S0141-3910\(98\)00146-3](https://doi.org/10.1016/S0141-3910(98)00146-3)

429 **Kozłowski, R.; Władysław-Przybylak, M. 2008.** Flammability and fire resistance of  
430 composites reinforced by natural fibers. *Polym Adv Technol* 19(6): 446-453.  
431 <https://doi.org/10.1002/pat.1135>

- 432 **Kurt, R.; Mengelolu, F.; Meric, H. 2012.** The effects of boron compounds synergists with  
433 ammonium polyphosphate on mechanical properties and burning rates of wood-HDPE  
434 polymer composites. *Eur J Wood Prod* 70(1-3): 177-182. [https://doi.org/10.1007/s00107-](https://doi.org/10.1007/s00107-011-0534-2)  
435 [011-0534-2](https://doi.org/10.1007/s00107-011-0534-2)
- 436 **Kumar, R.; Chandrashekar, N. 2014.** Fuel properties and combustion characteristics of  
437 some promising bamboo species in India. *J For Res* 25(2): 471-476.  
438 <https://doi.org/10.1007/s11676-014-0478-6>
- 439 **Kumar, R.; Gunjal, J.; Chauhan, S. 2021.** Effect of carbonization temperature on  
440 properties of natural fiber and charcoal filled hybrid polymer composite. *Compos B: Eng*  
441 217: 108846. <https://doi.org/10.1016/j.compositesb.2021.108846>Get
- 442 **Lee, S.Y.; Chun, S.J.; Doh, G.H.; Kang, I.A.; Lee, S.; Paik, K.H. 2009.** Influence of  
443 Chemical Modification and Filler Loading on Fundamental Properties of Bamboo Fibers  
444 Reinforced Polypropylene Composites. *J Compos Mater* 43(15): 1639–1657.  
445 <https://doi.org/10.1177/0021998309339352>
- 446 **LeVan, S.L. 1984.** Chemistry of fire retardancy. The chemistry of solid wood. In *Advances*  
447 *in chemistry series*: 207p. Rowell, R. (ed). American Chemical Society, Washington, D.C.,  
448 USA. <https://pubs.acs.org/doi/abs/10.1021/ba-1984-0207.ch014>
- 449 **Mouritz, A.P.; Gibson, A.G. 2006.** Flame Retardant Composites. In *Fire Properties of*  
450 *Polymer Composite Materials*: 237-286. Gladwell, G.M.L. (ed.). Springer, London, UK.
- 451 **Nagieb, Z.A.; Nassar, M.A.; El-Meligy, M.G. 2011.** Effect of Addition of Boric Acid and  
452 Borax on Fire-Retardant and Mechanical Properties of Urea Formaldehyde Saw Dust

453 Composites. *Inter J Carbohydrate Chem* Article ID 146763.  
454 <http://downloads.hindawi.com/archive/2011/146763.pdf>

455 **Palza, H.; Reznik, B.; Kappes, M.; Hennrich, F.; Naue, I.F.C.; Wilhelm, M. 2010.**  
456 Characterization of melt flow instabilities in polyethylene/carbon nanotube composites.  
457 *Polymer* 51(16): 3753-3761. <https://doi.org/10.1016/j.polymer.2010.06.016>

458 **Pan, M.; Mei, C.; Du, J.; Li, G. 2014.** Synergistic effect of nano silicon dioxide and  
459 ammonium polyphosphate on flame retardancy of wood fiber-polyethylene composites.  
460 *Compos Part A* 66: 128-134. <https://doi.org/10.1016/j.compositesa.2014.07.016>

461 **Panagiotou, T.; Levendis, Y.A. 1994.** Study on the combustion characteristics of PVC, poly  
462 (styrene), poly (ethylene), and poly (propylene) particles under high heating rates. *Combust*  
463 *Flame* 99(1): 53-63. [https://doi.org/10.1016/0010-2180\(94\)90082-5](https://doi.org/10.1016/0010-2180(94)90082-5)

464 **Salemane, M.G.; Luyt, A.S. 2006.** Thermal and mechanical properties of polypropylene-  
465 wood powder composites. *J Appl Polym Sci* 100(5): 4173-4180.  
466 <https://doi.org/10.1002/app.23521>

467 **Schneider, M.H.; Phillips, J.G.; Lande, S. 2000.** Physical and mechanical properties of  
468 wood polymer composites. *J Forest Eng* 11(1): 83-89.  
469 <https://doi.org/10.1080/08435243.2000.10702748>

470 **Shafizadeh, F. 1984.** The Chemistry of Pyrolysis and Combustion. In *The Chemistry of Solid*  
471 *Wood*. Advances in Chemistry Series 207: 489-529. Rowell, R. (ed.). American Chemical  
472 Society, Washington, D.C., USA. <https://pubs.acs.org/doi/abs/10.1021/ba-1984-0207.ch013>

473 **Stark, N.M.; White, R.H.; Mueller, S.A.; Osswald, T.A. 2010.** Evaluation of various fire  
474 retardants for use in wood flour–polyethylene composites. *Polym Degrad Stab* 95(9): 1903-  
475 10. <https://doi.org/10.1016/j.polymdegradstab.2010.04.014>

476 **Wang, Y.; Simonsen, J.; Neto, C.P.; Rocha, J.; Rials, T.G.; Hart, E. 1996.** The reaction  
477 of boric acid with wood in a polystyrene matrix. *J Appl Polym Sci* 62(3): 501-508.  
478 [https://doi.org/10.1002/\(SICI\)1097-4628\(19961017\)62:3%3C501::AID-APP8%3E3.0.CO;2-](https://doi.org/10.1002/(SICI)1097-4628(19961017)62:3%3C501::AID-APP8%3E3.0.CO;2-U)  
479 [U](#)

480 **Wang, Q.W.; Li, J.; Winandy, E.J. 2004.** Chemical mechanism of fire retardance of boric  
481 acid on wood. *Wood Sci Technol* 38(5): 375-389. <https://doi.org/10.1007/s00226-004-0246-4>

Accepted manuscript