Flame Retardant Synergism of GUP and Boric Acid by Cone Calorimetry

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ABSTRACT: Wood was treated with a new composite flame retardant (FRW), with its components guanyl urea phosphate (GUP) and boric acid (BA) to impart flame retardance. The flame retarding behavior of these samples was valued by cone calorimeter. The flammability parameters, including rate of heat release (RHR), total heat release (THR), effective heat of combustion (EHC), total mass loss (TML) and mass loss rate (MLR), yield of CO, smoke production rate (SPR), and specific extinction area (SEA) were recorded simultaneously. By analyzing these data, it was concluded that most combustion parameters of wood decreased by the treatment, especially for the FRW treatment, considerably decreased while the date for wood treated with GUP or boric acid decreased much less for the similar upload, which indicated a synergistic effect of flame retardance and suppressing smoke between GUP and boric acid in FRW, which has not been reported in other researches until now. Meanwhile, the probable flame retardation mechanism was proposed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5522–5527, 2006

Key words: cone calorimeter; flame retardant; FRW; synergistic effect; wood

INTRODUCTION

Wood, which mainly consists of cellulose, lignin, and hemicellulose, catches fire easily and burns vigorously with flame. The use of wood in house interiors, buildings or public transport constitutes a potential hazard for people in case of fire. The need for consumer protection, coupled with the new regulations and environmental concerns, increases the interest in flame-retardant treatments. Illustrative of various past approaches of imparting flame retardance of wood are treatments with compositions containing phosphorus and basic nitrogen compounds such as ammonium phosphate, melamine-phosphoric acid, urea-dicyandiamide-phosphoric acid and other phosphoric amines to accelerate the formation of a carbonized layer on materials.[1,2] Often formaldehyde is introduced to produce a phosphate salt of the methylolated guanyl urea to improve the stability and leach resistance of flame retardant.[3–5] However, there are some disadvantages associated with these before-mentioned compositions because of their use of formaldehyde, urea, and their ultimate pH. For example, formaldehyde may not be environmentally acceptable in some instances and urea is both known to be relatively corrosive and hygroscopic when employed in applied compositions at their applied pH ranges. The cost of the treated wood produced using these compositions is also relatively high.

A flame retardant of new formulation for wood (FRW), whose components are mainly guanyl urea phosphate (GUP) and boric acid, is generally environmentally acceptable; relatively low in toxicity, noncorrosive and nonhygroscopic, and which may be stored for relatively long periods of time.

In this work, wood was first treated with FRW, GUP, and boric acid, respectively. The flame retarding behavior of these samples was evaluated by cone calorimeter. The flammability parameters, including rate of heat release (RHR), total heat release (THR), effective heat of combustion (EHC), total mass loss (TML) and mass loss rate (MLR), yield of CO, smoke production rate (SPR) and specific extinction area (SEA) were simultaneously recorded to predict the course of the fire. From these data, the synergistic effect of fire retardance between GUP and boric acid was obvious, which has not been reported in any other research till now, and the probable flame retardation mechanism was proposed.

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TABLE I
Pk RHR and Max THR Values of Wood and Wood Treated with FR

Sample no.	FR	Retention (%; kg/kg)	2nd Pk RHR (kW m^2)	Decrease (%) Δ	Max THR (MJ/m^2)	Decrease (%) Δ
I	–	–	135	–	20.4	–
I	BA	33	100	26	17.3	15.2
III	GUP	31.4	81	35	13.3	34.8
IV	FRW	28.6	50	63	11.9	41.7

EXPERIMENTAL

Chemicals

To prepare the phosphate salt of the guanyl urea (GUP), water was taken in a container and agitated, while 85 g of dicyandiamide were added. 105 grams of phosphoric acid (85%) were subsequently added. The resulting mixture was heated to ∼ 85°C and held at that temperature for approximately 45 min. The mixture was then cooled to obtain an ∼ 13.5% aqueous GUP solution.

The FRW solution was prepared by first mixing 200 g of before-mentioned GUP solution and water together in an ∼ 1000 mL flask. Then 51.5 g of boric acid was added during the agitation of the flask. Agitation was continued for ∼ 30 min until the boric acid was dissolved. The pH of the solution was finally adjusted to about 4.75–5.25 with NaOH. These solutions were diluted with water till the prescribed concentration was reached before use.

Sample preparation

Specimens of larch (*North of China*) were planed timber in which cellulose amounts to about 45%, lignin and hemicellulose contents are 32 and 15%, respectively. The specific gravity was about 0.31, ash content was 5%, the moisture content was 7%, and volatile matter contents were 6%. Specimens were impregnated with chemicals for 2 h at 60°C under atmospheric pressure, and each sample was dried at 60°C. The retention (wt %) was measured for each sample. Sizes of samples were 100 mm L × 100 mm W × 3 mm T for the cone calorimeter. The samples I–IV, virgin wood and wood treated with the aqueous solution of boric acid (BA), GUP and FRW as flame retardants, respectively, are listed in Tables I–IV.

Cone calorimeter

The test method using the cone calorimeter was ASTM M 1354, *Standard Test Method for Heat Release Rates for Materials and Products Using a Consumption Calorimeter*.[6] Approximately 13.1 MJ of heat was released per kilogram of oxygen consumed. The external heat fluxes usually chosen were 35 kW/m^2 because it corresponds to a common heat flux in mild fire scenario fire. Our samples were exposed to a Stanton Redcroft Cone Calorimeter under a heat flux of 35 kW/m^2. The cone data reported in this work were the average of three replicated experiments.

RESULTS AND DISCUSSION

Heat release

RHR, THR, and EHC for samples I–IV are shown in Figures 1–3, and the corresponding values are listed in Table I and II.

From Figure 1, it is obvious that there are two peaks in the HRR curve of wood, which is closely related to its combustion characteristics. It is suggested that there are three stages of ignition, burning, and extinguishment in wood burning.[7]

During the ignition stage, wood gives off lots of combustible gases because of pyrolysis under the influence of external heat. As the concentration and temperature ascend and reach the ignition threshold value, combustible gases are ignited and react dramatically instantly, from which lots of heat is released, which produces as the first peak in the HRR curve. With the subsequent increase of specimen temperature, the pyrolysis process increases and the surface of wood begins to burn. Carbon residue is generated as a combustion product and piles

TABLE II
Pk EHC and Peak of CO Yield Values of Wood and Wood Treated with FR

Sample no.	FR	Pk EHC (MJ/kg) 1st	2nd	Decrease (%) Δ 1st	2nd	Pk CO yield (kg/kg)	Increase (%) Δ
I	–	8.5	80.0	–	0	0.048	–
II	BA	7.2	80.0	8.2	0	1.592	3220
III	GUP	6.0	80.0	29.4	0	0.556	1058
IV	FRW	5.2	40.4	38.8	49.5	0.245	410

TABLE III
Max TML and Pk MLR Values of Wood and Wood Treated with FR

Sample no.	FR	Max TML (%)	Decrease (%) Δ	Pk MLR (kg/s)		Decrease (%) Δ	
				1st	2nd	1st	2nd
I	–	81.5	–	0.098	0.142	–	–
II	BA	71.7	12.3	0.080	0.122	18.4	14.1
III	GUP	68.9	14.7	0.121	0.134	−23.5	5.6
IV	FRW	66.1	18.9	0.074	0.076	24.5	46.5

up on the surface until a layer of char is formed, which insulates the interior of wood from the external heat despite the high temperature that may occur on the surface. Therefore, a long period of steady process occurs that involves both pyrolysis gas combustion and carbon combustion. This steady period corresponds to the middle between the two peaks in curve. With the further elevation of temperature, cracks appear on the carbon residue, which allows pyrolysis products that are formed in the interior heated parts of the sample to escape through the surface, and thus accelerates the burning. This acceleration produces the second peak. The last part of the curve, after the volatiles are consumed, corresponds to the nonflame burning, i.e., glowing. Then the flame extinguishes.

It is apparent that the burning of the flame is most important in the growth and fully developed phases of the fire and corresponds to the intensity of the fire. The RHR was recognized to quantify the size of fire.[8] It is very clear that a significant flame retardant effect is obtained with treatment on wood. The peaks of RHR decrease by the treatment with flame retardants, especially for the second peak. Virgin wood shows a RHR peak (second) about 135 kW/m^2 while the RHR peaks of wood treated with GUP and boric acid are 81 and 100 kW/m^2. RHR peak decreased by 35% with 31.4% GUP and by 26% with 33% boric acid. It is suggested that the decrease of RHR with addition of GUP or boric acid is probably just due to dilution of combustible material (wood) with noncombustible materials (GUP or boric acid). For the wood treated with FRW, the RHR peak is only 50 kW/m^2. The RHR peak value is approximately greatly decreased by 63% with 28.6% retention. In comparison with samples II and III, the decrease of RHR peak of sample IV is much

higher, which shows that the RHR is much decreased, while the retention is not increased. It is clear that there is a strong synergistic effect of flame retardance between GUP and boric acid in FRW. It is well known that the samples containing phosphorus can release of phosphoric acid which catalyzes the dehydration and carbonization of wood, resulting in formation of less flammable products and correspondingly more char.[9] Meanwhile, boric acid relatively increases thermal stabilization of wood,[10] which suppresses the mass loss. FRW includes simultaneously GUP and boric acid. So their synthetical actions result in the synergistic effect of GUP and boric acid on flame retardance.

From Figure 1, we can also see that the second peaks for treated wood become flat and occur at longer time, especially for samples II and IV (about 320, 360s) while the first peaks almost do not shift. The heat release is distributed between two broad peaks covering a wide area, resulting in a major reduction in RHR and flammable products which fuel the flaming combustion reaction. This is another factor contributing to flame retardance.[11]

Figure 2 presents the THR for samples I–IV. The slope of THR curve can be assumed as representative of fire spread.[6] It is very clear that the flame spread of samples II–IV have decreased, and the flame spread of sample IV is comparatively the lowest. From the Table I, we can also see that the THR is decreased by the flame retardants. The maximum THR decreased by 15.2% with boric acid and by 34.8% with GUP while decreased by 41.7 with FRW for the similar upload. It is also suggested there is a synergistic effect of flame retardance between GUP and boric acid in FRW.

The EHC measured in the cone calorimeter corresponds mostly to the flame burning condition and

TABLE IV
Pk SPR and Pk SEA Values of Wood and Wood Treated with FR

Sample no.	FR	Pk SPR (m^2/s)		Dec. Δ (%)		Pk SEA (m^2/kg)		Dec. Δ (%)	
		1st	2nd	1st	2nd	1st	2nd	1st	2nd
I	–	0.0047	0.0138	–	–	452.7	139.6	–	–
II	BA	0.0096	0.0116	−104.3	15.9	641.9	149.2	−41.8	−6.9
III	GUP	0.0050	0.0068	−6.4	50.7	172.0	93.7	62.0	32.9
IV	FRW	0.0022	0.0011	53.2	92.0	86.1	24.3	81.0	82.6

Figure 1   Rate of heat release profile of samples I–IV.

Figure 3   Effective heat of combustion profile of samples I–IV.
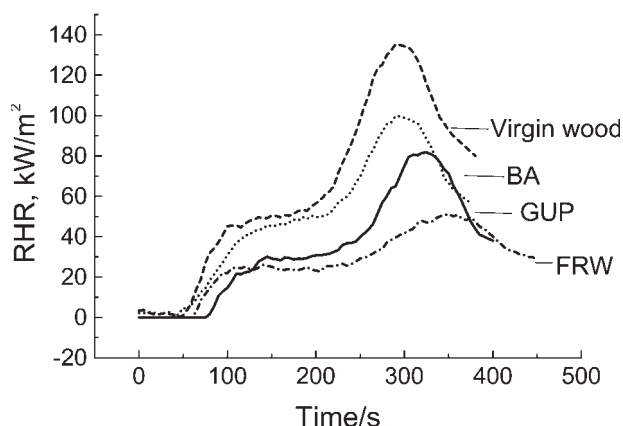
thus to combustion of volatiles from material. It is calculated from the ratio of values of THR and mass loss within specified time.[12] It is shown in Figure 3 and the values of peaks are listed in Table II. It is clear that the first peaks are all small ranging from 80s to 250s, and there is a very minor decrease with flame retardants as shown in Table II. Meanwhile, for the large (second) peaks of EHC for samples II-III are almost not decreased. However, the EHC value for sample IV is much lowered by 49.5% when FRW is present. This may be because of the synergistic effect of flame retardance between GUP and boric acid.

Mass loss

The TML and the MLR for samples I-IV are shown in Figures 4 and 5, and the corresponding values are listed in Table III.

   Generally, the function of flame retardant in wood is to increase the char at the cost of flammable volatile products.[11,13] So the more the char yield is, the better the flame retardant is. The TML (Fig. 4, Table III) gradually decreases for treated wood. The TML
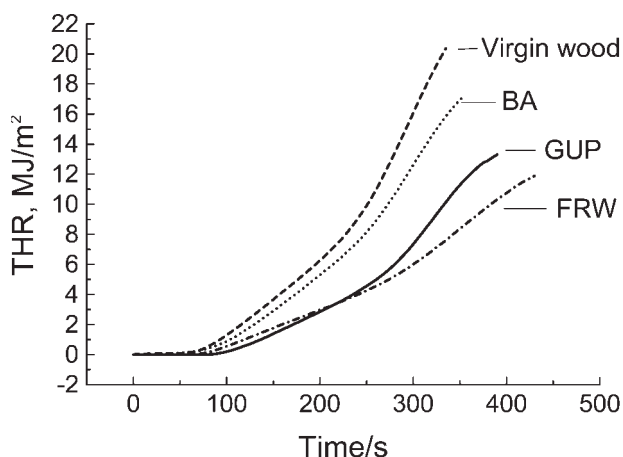
over the whole test for the virgin wood is 81.5% of the original mass. For the treated wood higher residues are left. In the case where FRW is used, the TML is 66.1% of the original mass, decreased by 18.9% while for BA and GUP used, decreased by 12.3% and 14.7%, respectively. This observation indicates a synergistic effect of flame retardance between GUP and boric acid in FRW. This is also supposed by MLR as shown in Figure 5 and Table III. Peaks of MLR are decreased by 24.5% and 46.5% for sample IV while the decrease is much less for samples II–III (−23.5%–18.4%).

Gas and smoke release

Carbon monoxide yield, SPR and average SEA of smoke for samples I–IV are shown in Figures 6–8, and the corresponding values are listed in Table II and IV.

   Generally, the smoke production and toxic gas formation along with the heat release rate play a critical
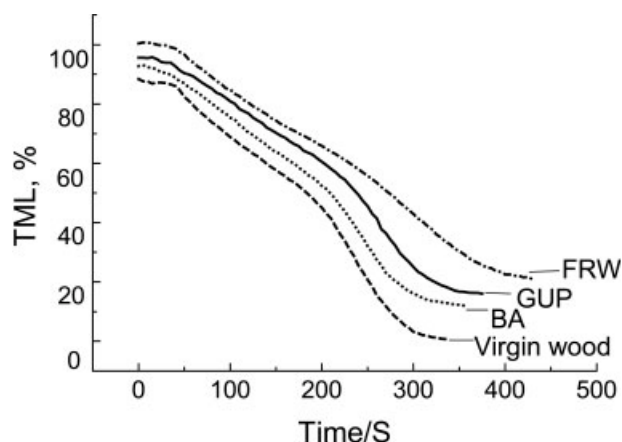

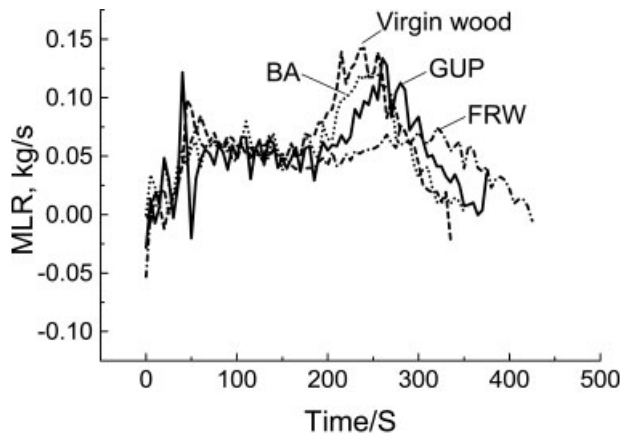**Figure 2**   Total heat release profile of samples I–IV.

Figure 4   Total mass loss profile of samples I–IV.

Figure 5 Mass loss rate profile of samples I–IV.

Figure 7 Smoke production rate profile of samples I–IV.

role in fire conditions.[14] One of most toxic gases released from burning wood is carbon monoxide. From Figure 6 and Table II, we can see that for the flame retardant wood (samples II–IV), carbon monoxide yield is much more than that of virgin wood. Usually, the flame retardant materials produce more carbon monoxide per mass unit burned than untreated materials. The carbon monoxide formation at the expense of carbon dioxide is however an important fire retardant principle.[14] In the case of sample containing FRW, the carbon monoxide yield is much lower than that of samples II–III in which CO yields are increased by 3220 and 1058% while increased by 410% for wood treated with FRW. This shows that the FRW decreases the formation of toxic carbon monoxide maybe because of the synergistic effect between GUP and boric acid on suppressing carbon monoxide.

The effect of flame retardant on smoke formation was measured. The SPR as the function of time is shown in Figure 7. For samples, smoke is formed first at the beginning of burning and shortly prior to the end of burning. The effect of BA and GUP is very little, especially for BA, and it increase the smoke release
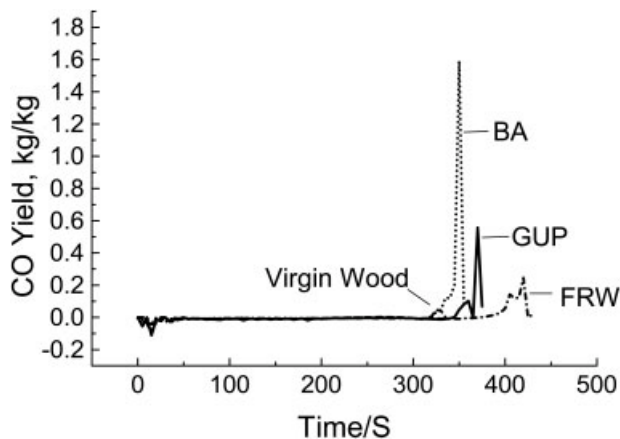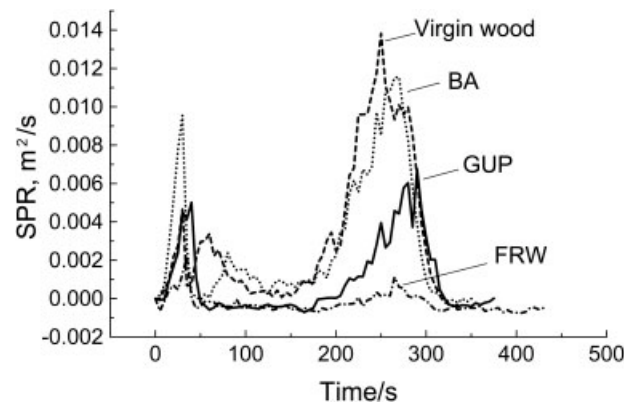
rate in some degree. However, the effect of FRW on smoke is quite obvious. The first peak of SPR is decreased by 53.2% and the second peak of smoke formation is even eliminated. This may also be attributed to the synergistic effect between GUP and boric acid on suppressing smoke. Similar result can be obtained from the average SEA of smoke profile in Figure 8. The SEA peaks of wood treated with BA increased by 41.8% and 6.9%, and for wood modified with GUP, the SEA peaks is decreased by 62.0% and 32.9%. However, for FRW treatment, it is much reduced to 81.0% and 82.6%. This also suggests the synergistic effect between GUP and boric acid.

SUMMARY AND CONCLUSIONS

The flammability parameters of wood treated with FRW, including RHR, THR, EHC, TML and MLR, yield of CO, SPR, and SEA, are considerably low while the date for wood treated with GUP or boric acid is much less for the similar upload, which indicates a synergistic effect between GUP and boric acid on flame retardance and suppressing CO and
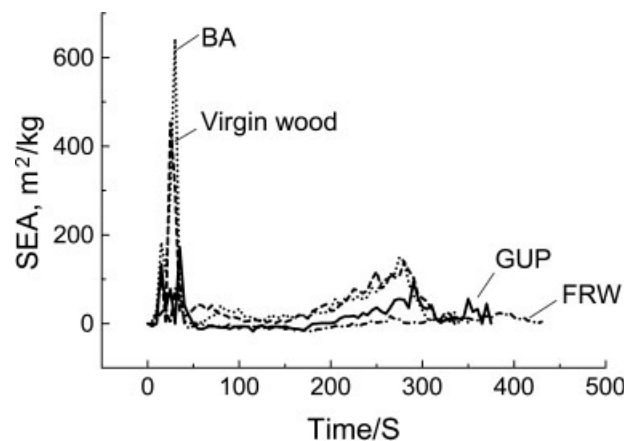

Figure 6 CO yield profile of samples I–IV.

Figure 8 Specific extinction area of smoke profile of samples I–IV.

smoke yield in FRW. It is proposed that GUP accelerates dehydration and carbonization of wood while boric acid relatively increases thermal stabilization of wood, and their synthetical actions result in more char and less flammable volatile products, obtaining a better flame retardance.

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