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EFFECTS OF DIFFERRENT BORON-BASED FLAME RETARDANTS ON THE COMBUSTIBILITY OF BAMBOO FILAMENTS

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ABSTRACT

In this study, eight types of boron-based flame retardants were performed to evaluate the effects of different boron components on the combustibility of the bamboo filaments. Disodium octaborate tetrahydrate, boric acid/borax, and nano-$ZnBO_4$ were used as the active flame retardant components. Besides, other inorganic flame retardants including nano-SiO_2 and ammonium polyphosphate (APP) were also introduced in order to increase the flame retardant of these boron-based components. The combustibility of the bamboo filaments treated with different flame retardants were evaluated by cone calorimeter analysis. The results showed that the flame retardants including the heat release and smoke release resistance of the bamboo filaments with different boron-based components and nano-SiO_2 or APP, could be significantly improved, especially, in the samples treated with the compound flame retardant composed of boric acid, borax and nano-SiO_2, which was attributed to the synergistic effect of these flame retardant components.

KEYWORDS: Bamboo filament, boron, flame retardant, smoke release, heat release.

INTRODUCTION

The bamboo industry has become more and more important in China, because the shortage of the wood resource with the implementation of the "Natural Forest Protection Project" has not satisfied the increasing needs of people (Sanchez-Monedero et al. 2018, Yao et al. 2019), while as the ideal alternative the accumulation volume of bamboo in China has more than 4.2 mil hm^2, which was the reason that China was known as the “Bamboo Kingdom” (Zhu et al. 2020, Tong et al. 2021). With the natural aesthetic characteristics, environmental ecology characteristics, shorter growth cycle and excellent mechanical properties, bamboo has been widely used in our life, such as in the furniture, building, decoration material, art work, etc. (Guzha et al. 2018, Guo et al. 2019, Tabassum et al. 2019, Tong et al. 2021). Predictably, as the wide application of bamboo, it could not only effectively save valuable forest resources (Hua et al. 2021), but also contribute to the low-carbon, environmentally friendly and sustainable development of the environment (Liu et al. 2020, Huang et al. 2020).

However, compared with the flammable material wood, bamboo was more flammable because the chemical components, such as the extract and ash content, were much higher (Zheng et al. 2019, Lin et al. 2021), which would cause serious fires to endanger people’s property and life safety (Wu et al. 2021, Lv et al. 2021). Therefore, it was critical to increase the flame retardant of bamboo with the reasonable flame-retardant modification treatments for its safe and wide applications (Fang et al. 2020, Wang et al. 2021). At present, the flame retardant treatments of bamboo in the market were mainly composed of the phosphorus-nitrogen components, which had many negative effects, such as the poor smoke release and more risks for human being (Wang et al. 2020, Li et al. 2021). Therefore, it is particularly urgent to develop an environmental friendly and efficient flame retardant. Boron-based flame retardants have many advantages compared with the traditional bamboo flame retardants, such as the excellent flame retardant, ideal antibacterial and insecticidal capabilities (Zhang et al. 2020, Jin et al. 2020), lower toxicity and prices (Chen et al. 2018). As the result, it was considered to be a promising furniture flame retardant with great development potential (Medlock et al. 2012, Li et al. 2021).

In this study, boron-based flame retardants such as disodium octaborate tetrahydrate, boric acid/borax, nano zinc borate ($ZnBO_4$), and inorganic carbon dioxide (SiO_2) and ammonium polyphosphate (APP) with excellent flame retardant were selected as the main active ingredients of the compound flame retardants. The effects of different flame retardant components on the heat resistant and smoke resistant of the treated bamboo filament were evaluated by cone calorimeter analysis.

MATERIAL AND METHODS

Samples

Moso bamboo (*Phyllostachys edulis* (Carr.) H.de Lehaie) was taken from Hubei Province, China. They were divided into bamboo slices, and the bamboo slices were evenly split in the thickness direction and then were woven and cut into a size of 10 mm (length) × 10 mm (width) × 2 mm (thickness) bamboo filaments.

Fire retardant treatments

The concentrations of the active ingredients in the flame retardant were expressed by their mass fraction in the solutions. The specific preparation conditions and figures were shown in Tab. 1. Among them, nano-SiO_2 and nano-$ZnBO_4$ need to be added with the co-solvent sodium polyphosphate (ratio 1:10) to make them completely dissolved in water. In addition, the samples treated in the factory which has passed the GB 8624 (2012) test and reached B1 level (nonflammable material) were used as the control group labeled as C as showed in Tab. 1. The flame retardants were introduced into the bamboo filaments by vacuum-pressure impregnation. The bamboo filaments were put in a closed vacuum pressurized tank, which was vacuumed to -0.1 MPa for 30 min, and introduced the flame retardant to the tank, then pressurized to 0.8 MPa for 1 h. After different flame-retardant treatments, the bamboo filaments were dried at 60°C, relative humidity of 80% to reach constant weight and prevent deforming.

Tab. 1: Components of different compound fire retardants.

Test N°.	Flame retardant composition	Concentration (%)
S0	Without treatment	0
C	Factory treatment	B1 level
S1	Boric acid/borax + nano SiO_2	20/0.2
S2	Boric acid/borax + ammonium polyphosphate	20/1.0
S3	Boric acid/borax + disodium octaborate tetrahydrate + ammonium polyphosphate	20/1.8/1.0
S4	Boric acid/borax + ammonium polyphosphate + nano-$ZnBO_4$	20/1.0/0.7
S5	Boric acid/borax + disodium octaborate tetrahydrate + nano SiO_2	20/1.8/0.1
S6	Boric acid/borax + nano SiO_2 + ammonium polyphosphate	20/0.2/1.0
S7	Boric acid/borax + nano-SiO_2 + nano-$ZnBO_4$	20/0.2/0.3
S8	Boric acid/borax + disodium octaborate tetrahydrate + nano SiO_2 + ammonium polyphosphate	20/1.8/0.2/1.0

Combustibility by cone calorimeter

The combustibility of the samples with different treatments as shown in Tab. 1 were selected and evaluated by a cone calorimeter according to ISO 5660-1 (2015). Six samples with the same treatment condition were prepared with dimensions of 100 mm (tangential) × 100 mm (longitudinal) × 1.5 mm (radial), and placed horizontally under a cone heater with a heat flux of 50 $kW \cdot m^{-2}$ (2000, Fire Testing Technology, U.K.). A stainless steel cover with an opening of 0.0088 m^2 on the upper part was attached. The data was recorded by a computer every second.

RESULTS AND DISCUSSION

Heat release analysis

Heat release rate analysis

As showed in Tab. 2, compared with the materials without any treatment (S0), all of the different flame retardants could be significantly reduced the peak heat release rate (HRR) of the bamboo filaments, especially for the samples in S2 condition, which was a little better than the B1 level of the treated samples (C).

The results indicated that compared with the phosphorus flame retardant, the boron-based flame retardants had better release resistant ability, which was consistent with the previous results that Li et al. (2021) had pointed that bamboo filaments treated with boric acid and borax could be significantly improved the flame retardant, especially for the samples with the promising hot and cold treatment, and promising pressure treatment, attributed to the more stable boron fixed in the bamboo filaments.

Tab. 2: HRR appendix of bamboo filament treated with different fire retardant treatments.

Heat release rate	S0	C	S1	S2	S3	S4	S5	S6	S7	S8
PkHRR ($kW \cdot m^2$)	1183.25	512.26	1179.67	1010.27	1246.46	1219.53	1128.32	1284.93	1165.26	1185.69
Average HRR ($kW \cdot m^2$)	290.77	216.05	209.83	214.62	217.33	217.67	213.41	232.62	222.08	213.76

In the pre-combustion period (0-30 s), with the exception of S7 and S8, the HRR of other flame-retardant treated samples were similar with or slightly lower than those of S0 and C, and the lowest value was observed in S2 group. In the mid-combustion period (30-50 s), the HRR of bamboo filaments with different flame retardant treatments decreased significantly than those in S0, but still higher than those in group C treated samples. In the late stage of combustion (after 50 s), the HRR of different flame-retardant treated bamboo filaments all dropped to a relative low level, while the heat release rate in the untreated wood was still very fast. It could be seen from the results that the addition of different boron-based flame retardants significantly changed the thermal decomposition process of bamboo filaments, which resulted in the higher heat release at a lower temperature. As showed in Fig. 1, the average HRR value that in the entire combustion process, the different flame retardant treated samples were significantly lower than the untreated samples, especially the four groups of S1, S2, S5, and S8 treated samples, however, all of the boron-based flame retardant treated samples were lower than the samples of C group.

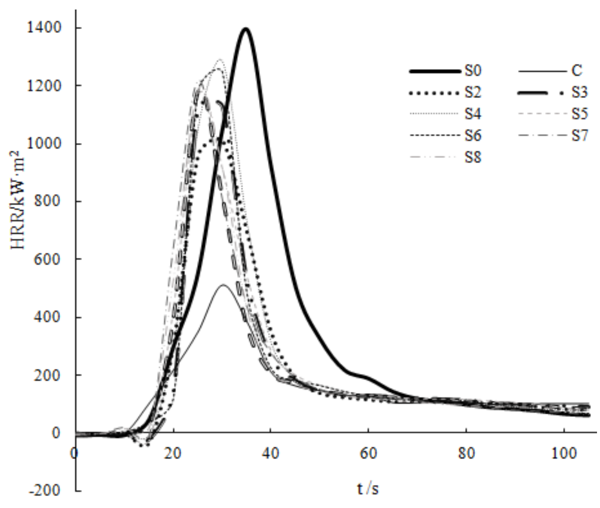

Fig. 1: HRR curves of different flame resistant treated bamboo filaments.

This result showed that for different inorganic flame retardants, although the initial stage of heat was not as good as that of the C group, as the combustion process continued, the synergistic effect among the different components would gradually manifested. This phenomenon was also explained by the flame retardant mechanisms of each flame retardant component. For example, under higher temperature conditions, the boron compounds generated glassy residues on the surface of the treated material to form a protective layer, which could effectively prevent further volatilization of the treated samples. Besides, boron-based compounds could accelerate the processing of the material into char, thereby reducing the high-temperature pyrolysis interval, which was reported by the previous studies that boric acid, borax, and nano-zinc borate can catalyze char formation during wood combustion, while APP would be decomposed by heat, undergo dehydration and heat absorption at different heating stages, promoted char formation, and dilute combustible gases (Chenet al. 2018).

Total heat release analysis

Compared with untreated samples, the total heat release (THR) of bamboo filaments treated with different boron-based flame retardants would be significantly reduced as shown in Fig. 2.

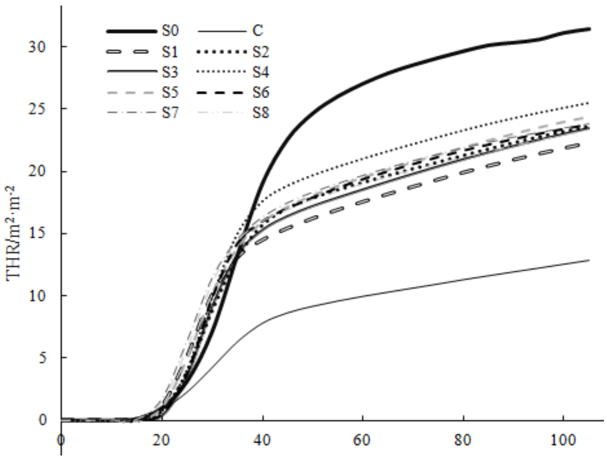

Fig. 2: THR curves of different flame resistant treated bamboo filaments.

In the early stage (0-40s), the total amount of heat was released quickly from the treated samples with different boron based compounds compared with the untreated samples and the control samples, which demonstrated that the boron compounds have changed the thermal decomposition path and accelerated the components of the bamboo filaments decomposed at lower temperature. In the late stage (after 40s), the total release of the samples treated with different boron compounds flame retardants was much lower than those untreated ones, which was attributed to the quick thermal decomposition in the early stage. Among them, the bamboo filaments with the best flame retardant was observed in the samples of S1 group, and its THR could be reduced by 10.07%, while the reductions of the other groups were 1.44-5.70%. Compared with the group C samples, the THR in the bamboo filaments treated with different boron-based flame retardants were still higher, even in the S1 group, which had the best heat retardant performance, the TSP was still about 70% higher than those of the C group. The result was consistent with other research (Su et al. 2021) that the heat release resistance of the boron based compounds should be improved by the modification with the other additives, such as the melamine polyphosphate (MPP) and hollow glass bead (HGB). It could be seen that, for different inorganic flame retardants, the synergistic effects of different components on the heat retardant of the bamboo filaments could be achieved through the reasonable compound conditions. However, how to reduce the heat release effectively was still a serious research project for boron-based flame retardant to treat bamboo filaments, and many efforts should be made in the researches of boron flame retardant fixation, treated procedures, compounding with other environmental flame retardants.

Smoke release analysis

As showed in Fig. 3, after different flame retardant treatments, the amount of smoke release of the bamboo filaments would be reached the peak value after 30 s burning, and then it would keep flat until the fire finished. Compared with untreated samples, even the S7 group with the highest total amount of smoke production (TSP) can be decreased by 75.64%, the S1 group with the lowest THR can be decreased by 88.79%, and for other groups the TSP would be decreased by 80.98 - 90.78%, which were very close to the C group. This result was consistent with our previous studies (Li et al. 2021) that boron flame retardants had excellent smoke resistant during combustion process of bamboo, because the boron-based compounds would be melted as a glass-like protective layer at higher temperatures and produce isolated charcoal effect.

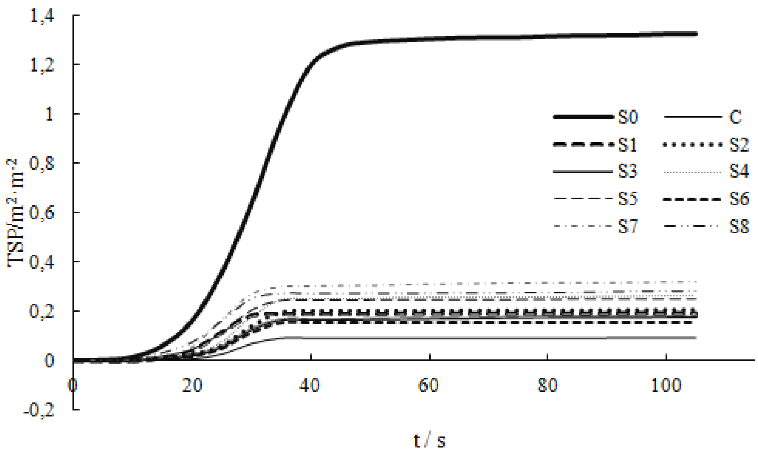

Fig. 3: TSP curves of different flame resistant treated bamboo filaments.

As showed in Tab. 3, compared with untreated samples, the visible smoke emission (ASEA) of the treated bamboo filaments could be significantly reduced. Among them, the lowest ASEA was observed in S1 group, and it could be decreased by more than 99%, and for S2 and S3 groups, the values of ASEA were very close to the C group.

Tab. 3: Smoke production appendix of different fire retardant treated bamboo filaments.

Smoke emission parameter	S0	C	S1	S2	S3	S4	S5	S6	S7	S8
ASEA/m^2•kg	195.08	16.00	10.40	18.83	18.92	34.23	47.43	36.96	34.07	45.21
Average CO yield ($kg•kg^{-1}$)	0.70	0.03	0.59	0.32	0.63	0.72	0.42	0.35	070	0.45
Average CO_2 yield ($kg•kg^{-1}$)	7.91	1.71	9.30	8.12	7.67	11.29	10.69	9.18	9.88	9.22

This result demonstrated that boric acid/borax composed with some inorganic compounds such as nano-SiO_2, disodium octaborate tetrahydrate, and / or ammonium polyphosphatethe with seasonable ratio could ensure the visible smoke emission from the treated samples in an extremely low level. However, different flame-retardant treatments had different effects on the yields of CO and CO_2. Compared with the untreated samples, except for the S4 and S7 groups, the CO yields of the other groups were much lower, but they were still much higher than C group, which showed that although different flame retardant components could promote the full combustion reaction of bamboo filaments, the synergistic effects of the flame retardant components were still not as thorough as the phosphorus, nitrogen and boron series of flame retardants. From the values of CO_2 yield, the yields of different boron-based compounds had been increased to different extents compared with the untreated samples and the samples in C group, which was also a potential safety hazard of boron-based flame retardants.

CONCLUSIONS

The combination of boron-based compounds with other inorganic flame retardant components could significantly change the thermal decomposition process of bamboo filaments, resulting in the reduction of the heat release rate (HRR), total heat release (THR) and smoke release (TSP) during fire process. The boron based flame retardant composed with some inorganic compounds with seasonable ratio could behave excellent flame retardant ability for bamboo filaments. Among them, the bamboo filaments with the best flame retardant was observed in the samples of S1 group, and its THR could be reduced by 10.07% and the TSP can be decreased by 88.79% compared to the untreated samples. In the future, many efforts would be still taken in order to improve the heat retardant of the bamboo filaments effectively.

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