COMBUSTIBILITY OF BORON-CONTAINING FIRE RETARDANT TREATED BAMBOO FILAMENTS

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Abstract. As an indoor decorative material, bamboo filaments should be treated with flame retardants for safe use. The effects of different treatment conditions on boron loading of flame retardants (boric acid/borax = 1:1) in bamboo filaments were investigated by single factor experimental design. Furthermore, effects of boron-containing flame retardants on combustibility of bamboo filaments were evaluated by cone analysis. The results showed that boron loading in treated bamboo filaments increased distinctly as treatment duration, temperature, or solution concentration increased. Compared with untreated and ultraviolet (UV)-treated bamboo filaments, heat release decreased obviously in treated bamboo filaments with greater boron loading, heat rates were only 50% and 30% of untreated bamboo filaments and UV bamboo filaments, and the total amount of heat release was decreased by 39.7% and 56.5%, respectively. During the combustion process, boron-containing flame retardants had excellent smoke suppression efficacy and total smoke release was

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decreased by 86.1% and 91.1%, respectively. As a result, boron-containing flame retardants promote carbon residue production of treated bamboo filaments and decrease the mass loss during fire.

Keywords: Bamboo filament, boric acid, borax, heat release, smoke release.

INTRODUCTION

As a renewable and natural material, bamboo has become the ideal substitute for wood in China's lack of forestry resources. Compared with wood, bamboo has many advantages. For example, it has a shorter growth cycle, higher yield and mechanical strength, better dimensional stability, and unique visual aesthetics (Zhao et al 2010). Therefore, bamboo-based materials have been widely used across China and other regions (Lei et al 2004; Yang et al 2007; Zhang 2011). Bamboo filaments, as one of the bamboo products, have not only the special decorative features of bamboo, which are superior to other materials, but also have their own unique characteristics. The excellent flexibility and smaller thickness, which make them arbitrarily curved and form various flexible shapes, allow the designers to express their thoughts and feelings directly and sufficiently in their works with bamboo filament. Also, as an indoor decorative material, bamboo filament can be applied to the wall quickly and removed or reused conveniently. Thus, the application process is environmentally safe. Therefore, bamboo filaments were originally used for indoor decoration to replace traditional decorative materials such as paints and wallpapers (Song et al 2014) and have achieved favorable effects on decorating and beautifying the living environment.

Fire safety is one of the most important concerns in all types of construction. Unfortunately, bamboo-based materials, especially bamboo filaments, burn much more easily when exposed to heat and air or strong heat radiation (Yang and Qing 2014) compared with wood-based materials. One possible reason is the difference in their chemical compositions. The content of extracts is rather high in bamboo compared with wood, which results in the significant difference in the pyrolysis process (Uysal and Ozciftci 2004; Blasi et al 2007; Terzi et al 2011) and the poorer fire resistance of bamboo filaments. The other possible reason is attributed to the thinner and smaller unit of bamboo filaments. Some studies (Li et al 2012) pointed out that the greater the material section, the greater the specific heat capacity, which means a smaller unit, such as a bamboo filament, needs less energy to reach the fire point. The greater the material section, the smaller the thermal expansion capacity, which means the internal stress caused by heat is also smaller. The surface of materials with greater section more easily forms the charring layer, which could stop oxygen supply and consume a lot of heat. Also, the greater the material section, the lower the thermal conductivity.

The thermal degradation of bamboo is mainly caused by the thermal degradation reaction of chemical components in cell walls, and it occurs in three different stages: the dehydration process, hemicellulose pyrolysis, and cellulose and lignin pyrolysis. At 80-220°C, the mass of bamboo decreased slightly, which was primarily caused by the evaporation of moisture in the bamboo. At 250-360°C, the mass of bamboo decreased dramatically because of the thermal degradation of the hemicellulose, cellulose, and extractives. During this period, the curve exhibited two major exotherms near 300 and 340°C, which were associated with the dehydration and thermal degradation of cellulose. Lignin was decomposed slowly through oxidation (Lee and Wang 2006; Zhu and Huang 2009). Above 360°C, the rate of mass loss was decreased slowly and accompanied by the residue carbon and volatile gases (Jiang et al 2011). When the temperature was up to 500°C, the degradation reaction was almost completed. The exact products of thermal degradation greatly rely on the degradation stages at which different heating rates and temperatures applied.

Based on GB (2012), bamboo is a combustible material (Zhu and Huang 2009). As a result, it is necessary to treat bamboo with suitable fire retardant chemicals to ensure its safe use as an indoor decorative material. Studies on bamboo fire retardants are limited, but studies on wood fire retardants can be used as references. The use of inorganic salts, such as monoammonium phosphate, ammonium sulfate, zinc chloride, and diammonium phosphate, as the treatment to render wood fire retardant was developed approximately 80 yr ago (Wang et al 2004). Liu et al (2013) also showed that a crushed bamboo mat treated with ammonium polyphosphate exhibited good fire retardant performance. These fire retardant treatments may affect wood adversely in various ways (increase hygroscopicity, decrease mechanical strength and dimensional stability, accelerate metal fastener corrosion, cause adhesion problems, increase abrasiveness, and leaching of fire retardants) (Taghiyari 2006). Most importantly, many of these effective chemicals are not suitable for indoor application because they could produce noxious and toxic smoke and gases from the treated products during the combustion process, which would interact with light to obscure vision (White and Dietenberger 1999). In addition, boron has low mammalian toxicity but remarkable plant toxicity and is effective as an insecticide and fungicide (Yalinkilic et al 1999), and also boron compounds are the basic components of many fire retardants for wood and other cellulosic materials (Nussbaum 1988). Borax tends to decrease flame spread, but it can promote smoldering or glowing. Conversely, boric acid suppresses glowing but has little effect on flame spread. Consequently, borax and boric acid are generally used together (LeVan 1984). Boric acid and borax mixtures have some efficacy in retarding flame spread on wood surfaces. In addition to the usual char-forming catalytic effect, they have a rather low melting point and form glassy films when exposed to high temperatures during the combustion process (Yang and Qing 2014). Yang and Qing (2014) also showed that borax and boric acid flame retardants decreased the maximum thermal degradation rate, shortened the pyrolysis interval, and promoted the residue carbon production of treated bamboo compared with untreated bamboo.

Nevertheless, the research on bamboo-based materials treated with boron-based fire retardant is rather scanty because of their lower loading and poor leaching performance. The aim of this study was to clarify the effects of immersed conditions (duration, temperature, solution concentration) on the boron loading (BL) and combustion performance in a boron-containing fire retardant treated bamboo filament, and the objective of this study was to provide useful fire retardant treatment information for bamboo filaments used as indoor decorative material.

MATERIALS AND METHODS

Samples and Treatment

Moso bamboo (*Phyllostachys edulis* (Carr.) H. de Lehaie) was taken from Hubei Province, China. After air drying, the moso bamboo was cut along the direction of the fiber to get many pieces of bamboo splits, and then bamboo filaments were drawn from the bamboo splits by a drawing machine as shown in Fig 1. The filaments were stuck together with nonwoven fabric by polyvinyl acetate adhesive and cut into small pieces with dimensions of 100 mm (tangential) $\times$ 100 mm (longitudinal) $\times$ 1.5 mm (radial). Bamboo filaments with similar weights were selected as test samples. The boron-based fire retardant was made up of 50% boric acid and 50% borax. The concentrations used in this study were 5, 10, and 20% (w/w), respectively. The effects of immersed durations, solution temperatures, and concentrations on the BL were determined by the single factor design shown in Table 1. The percentages of BL in the samples were calculated using the following equation, and the values were recorded in Table 1.

$$\mathrm{BL} = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (1)$$

where W_1 and W_2 are the weights of each specimen before and after the boric acid/borax treatment.

Fire Test

After fire retardant immersion, the bamboo filaments were dried at room temperature. One group of untreated samples with just ultraviolet (UV)

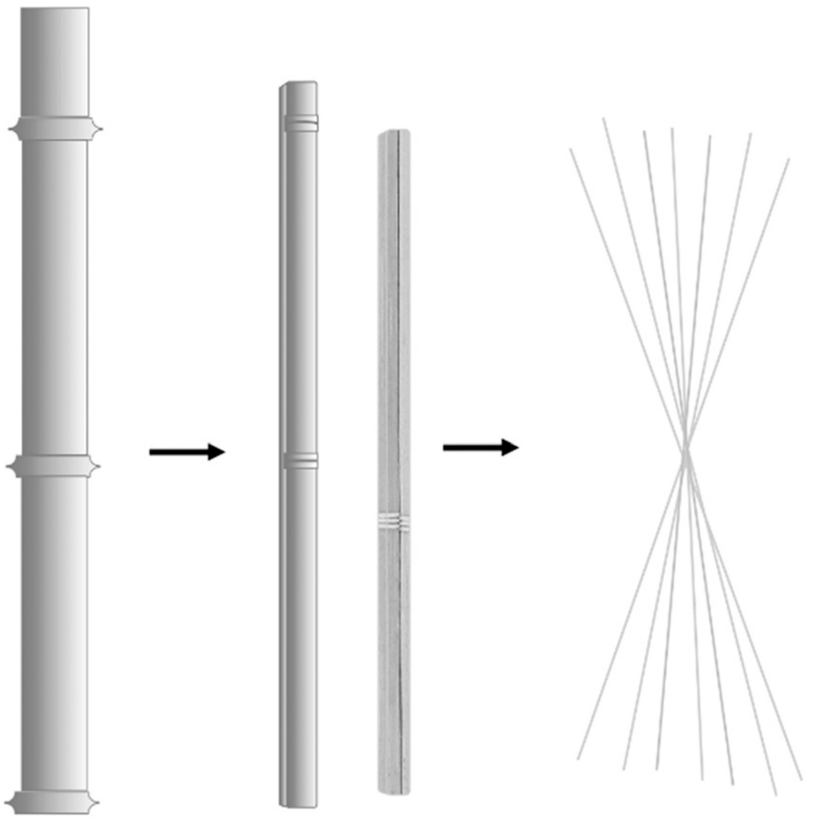

Figure 1. Diagram of the preparation of bamboo filaments.

finishing taken from a bamboo filament plant was used for reference. The fire performance of the specimens with different treatments as shown in Table 2 was evaluated by a cone calorimeter according to ISO (2002). Six specimens with the same treatment condition were prepared with dimensions of 100 × 100 × 1.5 mm and placed horizontally under a cone heater with a heat flux of 50 kW/m^2. A stainless steel cover with an opening of 0.0088 m^2 on the upper part was attached. The data were recorded by a computer every second. Specimens with different treatments were selected for the cone calorimeter tests as shown in Table 2.

Table 1. Single factor experimental design.

Concentration of boron based fire retardant (%)	Temperature (°C)	Duration (h)	Boron loading (%)
20	20	2	5.92
	40		6.97
	60		7.69
	100		10.70
20	60	0.5	6.61
		1	7.70
		2	7.69
		4	9.33
5	60	2	2.53
10			4.67
20			7.69
25			9.51

Table 2. Cone experimental conditions.

No.	Concentration of boron fire retardant (%)	Temperature (°C)	Duration (h)	Ultraviolet finishing(Y/N)	Boron loading (%)
T1	5	20	2	N	2.02
T2	20	60	2	N	9.64
T3	20	100	2	N	11.25
T4	—	—	—	N	—
T5	—	—	—	Y	—

RESULTS AND DISCUSSION

Treatment Conditions on BL Analysis

The effects of different treatment conditions on BL in treated bamboo filaments were evaluated in Fig 2. BL could be increased as concentrations, treatment temperatures, or treatment durations increased. Among them, the trend of BL in treated bamboo filaments changed much more obviously as the concentration changed compared with the other treatment conditions (Fig 2a). However, the solubility of boric acid/borax mixture was too low at room temperature, as proven by Zhang (2013). The highest solubility can only reach 20%, and the boron compounds would be deposited when the concentration exceeds this point, which is the same result observed in this study.

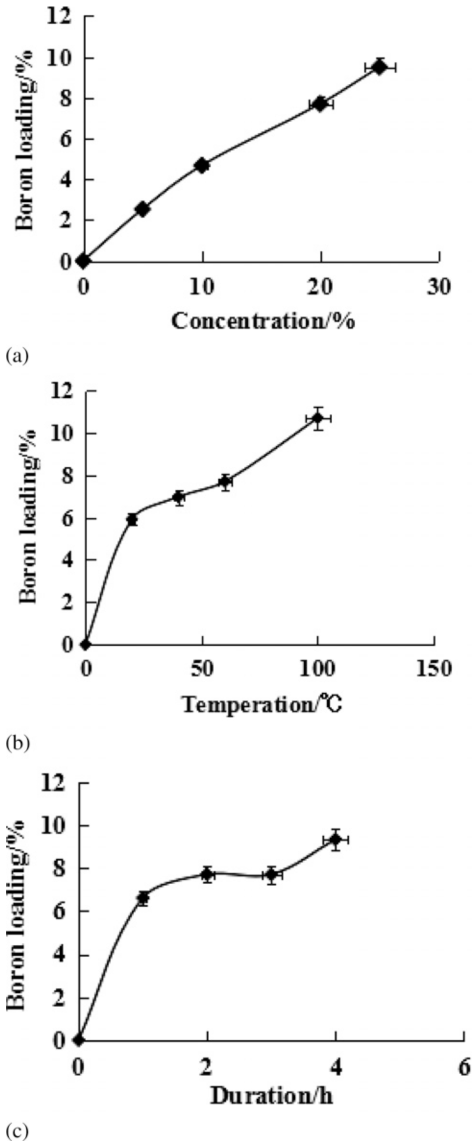

Figure 2. Effects of different treatment conditions on boron loading in the treated bamboo filaments. (a) Fire retardant concentrations, (b) treatment temperatures, and (c) treatment durations.

As shown in Fig 2b and 2c, 100°C was a promising key point treatment temperature for the bamboo filaments. At which point, the BL can reach to more than 10% only for the 2-h immersion treatment and was greater than the samples immersed in 60°C solution for 4 h. These results demonstrated that a higher temperature could act as a catalyst, which positively promoted the chemical and physical reactions between boron compounds and bamboo components. For the physical reactions, the higher treatment temperature increased the kinetic energy of the boron compound molecules and accelerated their penetration rate into the treated bamboo filament. At the same time, more extractives in the treated bamboo filaments were dissolved in hot water. As a result, the permeability of the treated bamboo filaments was improved greatly. For the chemical reactions, on one aspect, at 100°C, boric acid could be converted to metabolic acid with smaller molecular weight by dehydration reaction and decrease the permeability difficulty. On the others, the higher treatment temperature could accelerate the chemical reactions between bamboo filament components and boron compound molecules, although the formation of products has not been clearly investigated. Figure 2c represents the whole process of boron compounds penetrating into the bamboo filaments. The rate of BL increased at three different stages. In the first stage (0-1 h), the fire retardant penetrated sharply into the intercellular and cell lumen of the bamboo filaments. In the second stage (1-3.5 h), there was a leveling off of boron absorption. In the third stage (after 3.5 h), the boron compounds began to diffuse deeply into the fiber.

Fire Retardant Analysis

Heat release analysis. The heat release rate (HRR) and the peak of HRR (pkHRR) are two of the most important parameters to characterize fire behavior. The greater the HRR and pkHRR values are, the faster the pyrolysis and flame spread rate are during the combustion process. Figure 3 shows that the greatest HRR was found in the untreated bamboo filaments with UV finishing (T5), and the HRR was also much greater in the untreated bamboo filaments (T4) than in other boron-treated samples. The most promising result was observed in the samples with the greatest BL (T3), which were immersed in 20% boron compound fire retardant solution at 100°C for 2 h. A similar result was also observed in Table 3, which showed that the maximum pkHRR was obtained in the samples treated with UV paint (T5) and the pkHRR in the samples with the greatest BL (T3) decreased by 40% compared with the untreated samples. These results demonstrated that boron compounds efficiently and effectively improved the fire resistance of bamboo filaments. The reason is attributed to the property of boron compounds that could form molten B_2O_3 films at higher temperature, which could spread on the surface of the material and isolate oxygen and fire effectively (Yang and Qing 2014). Additionally, the boron compounds could release the bound water that cools the material and absorbs heat during fire (Enyu and Minxiu 1988; Marosi et al 2002; Silvo et al 2007). Based on results from Fig 3a and Table 3, bamboo filaments with UV finishing, which are widely used in the marketplace, are more flammable and conceal huge fire risk for their applications.

Table 3. Peak of heat release rate (pkHRR) from treated bamboo filaments with different treatments.

Sample	T1	T2	T3	T4	T5
pkHRR/(kW·m^2)	455.5	395.5	352.0	585.2	796.7
Time to peak/s	85	40	40	135	138

The total amount of heat release (THR) was used to evaluate the amount of heat release per unit of the material during the combustion process. The higher the amount of heat release, the greater the fire risk. Figure 3b shows, at the same fire stage, that the THR values in the samples without boron treatment (T4 and T5) were much greater than these treated samples. The most promising result was also observed in the samples with the greatest BL (T3). Figure 3b shows that the curves could be clarified into two different phases. The first phase (0-200 s) involved the fast thermal decomposition of the bamboo filament, and the second phase (200-800 s) involved the slow thermal decomposition and the formation of the carbon film. From the results, it appears that different fire retardant treatments had obvious effects on the combustion phases. This was attributed to the better fire resistant performance in the samples with the greater BL; and in another aspect, at

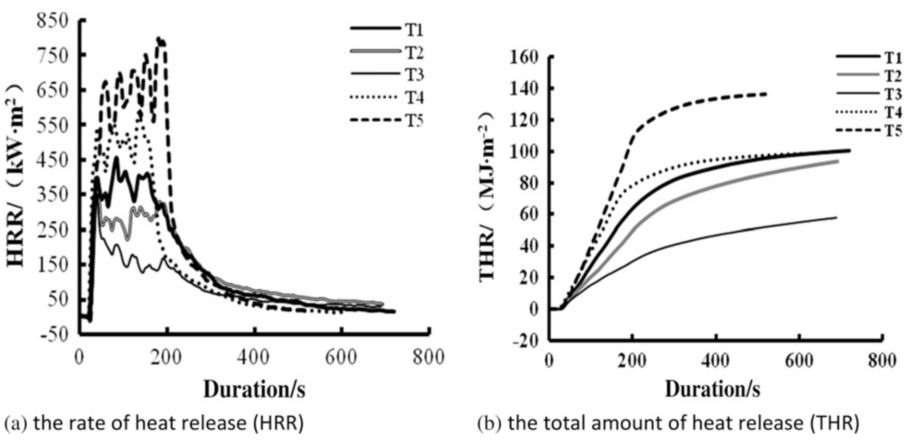

Figure 3. Heat release rate (HRR) of bamboo filaments with different treatments. (a) The HRR and (b) the total amount of heat release (THR).

higher temperature, boron compounds could have a much more stable reaction with the chemical components of bamboo filaments.

Smoke and toxic gas release analysis. Smoke and toxic gases released from the combustion process are the most critical reasons for personal injury and death in a fire. Total amount of smoke release per unit (TSP) of the material during a fire and average amount of smoke release per mass (ASEA) of the material during a fire are two important parameters to evaluate smoke release from a fire. As shown in Fig 4 and Table 4, compared with untreated and only UV-painted samples, TSP and ASEA were decreased dramatically in the boron-treated bamboo filaments even in samples with the lowest BL (T1). For samples with the greatest BL (T3), TSP was decreased to only 0.08 m^2 and ASEA was decreased to 0.281 $m^2 \cdot kg^{-1}$, whereas the values were 1.82 m^2 and 45.4 $m^2 \cdot kg^{-1}$ in the untreated samples (T4 and T5, respectively). The excellent smoke suppression of boron compound fire retardant has also been proven by many studies (Wang 2000; Mukherjee and Ansuman 2002) in which boron compounds were chosen to decrease the smoke release of some fire retardant formulas. The reason for the better smoke suppression is that boron could rapidly form a film on the surface of the material to impede smoke release.

More CO is produced from bamboo filaments during the insufficient combustion, which is the most common cause of death during a fire. Table 4 shows average CO production, especially for the samples with greater BL. A similar phenomenon was found for average CO_2 production. The results demonstrated that boron compounds aided in decreasing the properties of insufficient combustion and CO production. Therefore, boron compounds were found to indeed contribute to excellent smoke suspension and can decrease toxic gas production effectively.

Table 4. Smoke generation parameters of bamboo filaments with different treatments.

Sample	T1	T2	T3	T4	T5
ASEA/(m^2/kg)	25.50	4.60	0.28	45.40	53.40
Average CO production (kg/kg)	0.05	0.03	0.04	0.07	0.05
Average CO_2 production (kg/kg)	2.41	2.05	1.56	2.13	2.24

ASEA, average amount of smoke release per mass of the material.

Mass loss analysis. The mass loss curves of treated bamboo filaments reflected the thermal decomposition behaviors and the residue contents in the given phase during the combustion process, in which the level of combustion difficulty of the material in the same fire condition can be estimated. Figure 5 shows that the mass loss curves of all samples during fire can be clarified into two different phases. For the first phase, the mass of the bamboo filament decreased sharply, which was attributed to the rapid flame combustion.

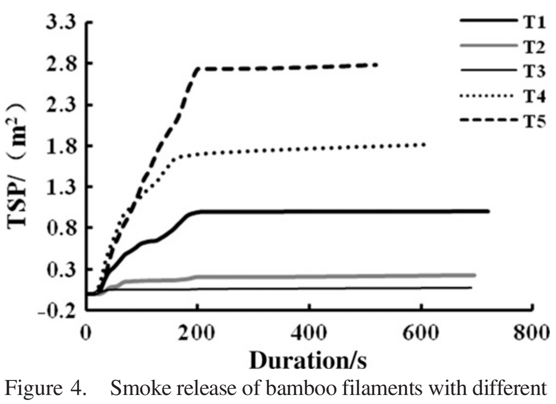

Figure 4. Smoke release of bamboo filaments with different treatments (TSP, total amount of smoke release per unit).

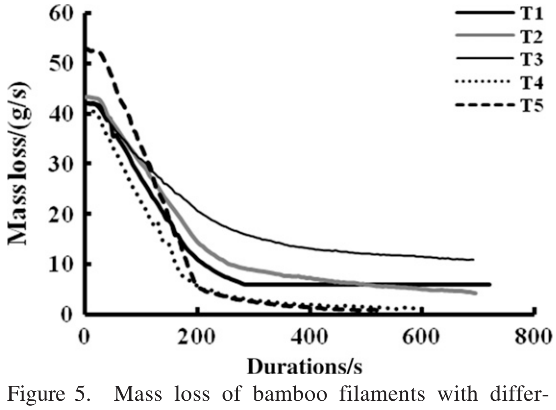

Figure 5. Mass loss of bamboo filaments with different treatments.

Mass decreased calmly in the second phase corresponding to the nonflame combustion. For samples with different treatments, the process of mass loss had significant differences. In the first phase, the greatest mass loss was observed in UV-treated samples, which was the result of rapid combustion of the UV film, which produced a lot of heat during the combustion process. The second mass loss was observed in the untreated samples, in which combustion rate was also very fast. The UV samples and untreated samples showed completely the same tendency of mass loss and nearly approached zero at the end of the fire of the second phase. However, for the samples treated with boron compounds, the mass loss changed much more slowly and the duration of the first phase (flame fire) was prolonged especially for the samples with the greatest BL (T1). This was caused by the film structure the boron compounds formed, which effectively prevented fire spread.

CONCLUSIONS

Bamboo filaments are easily destroyed by fire because of their chemical components and small size. During the combustion process, bamboo filaments produce abundant toxic smoke and gases, which are lethal to human beings. Boron-containing compound is very useful for modifying the indoor decorative material bamboo filament to increase its flame retardance and ensure its safe use. BL in treated bamboo filaments increased distinctly as the treatment duration, temperature, or solution concentration increased under atmospheric pressure. Compared with untreated and UV-treated bamboo filaments, thermal release decreased obviously in the treated bamboo filaments with greater retention. During the combustion process, boron-containing flame retardants had excellent smoke suppression efficacy and total smoke release was decreased by 86.1% and 91.1%, respectively, which is very critical for safe use as an indoor decorative material. Also, boron-containing flame retardants promoted carbon residue production of treated bamboo filaments and decreased mass loss during the combustion process.

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