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PROMOTION EFFECT OF NANO-SIO_2 ON HYGROSCOPICITY, LEACHING RESISTANCE AND THERMAL STABILITY OF BAMBOO STRIPS TREATED BY NITROGEN-PHOSPHORUS-BORON FIRE RETARDANTS

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ABSTRACT

Whereas hygroscopicity an leaching resistance often have a bad influence on performance of fire-retardants, in this work, nano-SiO_2 sol was added to different nitrogen-phosphorus-boron fire retardants to make four new compounds to impregnate bamboo strips, named: (1) ammonium dihydrogen phosphate + disodium octaborate tetrahydrate (AD), (2) ammonium dihydrogen phosphate + disodium octaborate tetrahydrate + nano-SiO_2 sol (ADS), (3) ammonium dihydrogen phosphate + boric acid (AB), and (4) ammonium dihydrogen phosphate + boric acid + nano-SiO_2 sol (ABS). After that, the hygroscopicity, leaching resistance and thermal stability were studied by scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDX), thermogravimetric (TG) and fourier-transform infrared spectrometer (FTIR), and the optimal compound fire retardant is ABS. The results show that the addition of nano-SiO_2 sol can not only reduce the hygroscopicity of fire-retardant bamboo strips effectively, but also improve its leaching resistance. The results also indicate that compared with non-fire-retardant bamboo strips, the thermal stability of bamboo strips treated with AB and ABS was improved significantly, and there was no significant difference between AB and ABS.

KEYWORDS: Bamboo, hygroscopicity, leaching resistance, thermal stability, compound fire retardant.

INTRODUCTION

China has rich bamboo resources, a wide range of bamboo products, and bamboo materials are increasingly used in construction, furniture and decoration or other fields (Li et al. 2016a). But bamboo materials are combustible, which means easy to burn, and with the rapid growth of consumption of bamboo products, the hazard of burning will increase, which may increase the security risks. So, it is necessary to apply fire retardant treatment of bamboo materials (Du et al. 2016). The most effective and commonly used method for fire-retardant treatment of bamboo materials is to add fire retardants (Li et al. 2017, Li et al. 2019). Currently, the fire retardant materials used in bamboo materials are mostly water-based inorganic fire retardants (Zheng et al. 2016), which are mainly due to its advantages like remarkable fire retardant effect, less pollution and low-cost (Zhang et al. 2014). Commonly used water-based fire retardants are ammonium dihydrogen phosphate, diammonium phosphate, ammonium polyphosphate, and boric acid, etc. (Xue et al. 2006). But they all have a certain degree of hygroscopicity, which can make them absorb water molecules and dissolve in water before they gradually lost in high humidity conditions (Na et al. 2009, Zhou et al. 2018, Yao et al. 2019). At the same time, the loss of fire retardants will inevitably lead to a corresponding reduction in fire retardant properties of bamboo materials. Therefore, the hygroscopicity and leaching resistance of water-based fire retardant and fire retardant bamboo materials cannot be ignored in the study of fire-retardant treatment of bamboo materials.

Nano-SiO_2 sol is a colloidal solution with a micelle diameter of 10-100 nm, and it has adsorption and blocking action when dried and solidified into gel (Lou et al. 2010), which shows a porous structure when added to the interior of the material. Meanwhile, nano-SiO_2 and nitrogen-phosphorus fire retardants can play a synergistic role in fire retardant and smoke suppression properties (Zhu et al. 2014, Altun et al. 2010). What is more, nano-SiO_2 gel has large specific surface area and strong adsorption properties, which may help to prevent water-based fire retardant from running off.

Some researchers have focus on the hygroscopicity and leaching resistance of wood materials treated by various fire-retardants. Zhang et al. (2015) synthesized a novel Al-Si-N-P water-soluble fire retardant, demonstrating the reduction of hygroscopicity and the improvement of leaching resistance of treated poplar wood. Pan et al. (2014) found that a protective and hydrophobic nano-SiO_2 sol layer on wood cells has a beneficial effect on improving hygroscopicity and reducing water uptake. Chu et al. (2017) found that heat treatment of NP treated wood can decrease the moisture absorption performance and enhance the leaching resistance and thermal stability. However, most of these researches are related to wood (Son et al. 2012, Kartal et al. 2007, Zhang et al. 2016, Li et al. 2016b), and bamboo has a unique microstructure that wood does not have: the vascular bundles are arranged in parallel in the longitudinal direction, the texture is consistent, and there is no horizontal organization such as wood rays (Du et al. 2010).Therefore, water-based fire retardants are more likely to escape from bamboo than wood. As mentioned above, since nano SiO_2 sol has the advantage of low hygroscopicity and strong leaching resistance, and limited research about hygroscopicity, leaching resistance of fire-retardant bamboo materials has been conducted. Therefore, the aim of this paper is to present a new optimal compound fire retardant, which can improve the hygroscopicity, leaching resistance and thermal stability of treated bamboo materials significantly when compared with common nitrogen-phosphorus-boron fire retardants.

MATERIALS AND METHODS

Materials

Bamboo strips (100 × 20 × 5 mm, L × W × T, MC: ~10%) without knots were purchased from Zhejiang Yongyu Bamboo Industry Limited by Share Ltd, Huzhou city, Zhejiang province, China. Ammonium dihydrogen phosphate (ADP) (99%) and boric acid (BA) (99.5%) were purchased from Sino Pharm Chemical Reagent Co., Ltd, Shanghai, China. Disodium octaborate tetrahydrate (DOT) were purchased from Zhengzhou Chengrui Chemical Products Co., Ltd, Zhengzhou City, Henan province, China. Nano-SiO_2 sol (SS) was obtained from Shaoxing Shangyu Jiangfeng Chemical Co. Ltd, Shaoxing City, Zhejiang province, China.

The names of four compound flame retardants are as follows: ammonium dihydrogen phosphate + disodium octaborate tetrahydrate (named AD), ammonium dihydrogen phosphate + disodium octaborate tetrahydrate + nano-SiO_2 sol (ADS), ammonium dihydrogen phosphate + boric acid (AB), and ammonium dihydrogen phosphate + boric acid + nano-SiO_2 sol (ABS). Four compound fire retardant solutions were modulated to the concentration of 20% according to the ratio of m(ADP) : m(DOT) = 7:3(AD), m(ADP) : m(BA) = 7:3(AB), m(ADP) : m(DOT) : m(SS) = 11:4:5(ADS), and m(ADP) : m(BA) : m(SS) = 11:4:5(ABS).

Preparation of bamboo strips impregnated by four compound fire retardants

Bamboo strips specimens were treated with four different compound fire retardants by impregnation method. The mass of each sample was measured after air drying in an oven at 103 ± 2°C for 12 h to ascertain their anhydrous mass. The prepared solutions of AD, AB, ADS and ABS were used to impregnate bamboo strips specimens at 50°C under normal atmospheric pressure for 4 h, respectively, while H_2O was used to impregnate bamboo strips at the same condition as control group. After that, the impregnated specimens were displaced at room temperature for 7 days, and then displaced in an oven at 103 ± 2°C for at least 12 h to ensure sufficient dryness.

Drug dosage calculation

The mass of each specimen was measured after each preparation step. The drug dosage (the amount of four compound fire retardants in treated specimen) (ASTM D3201/D3201M: 2013) was calculated according to Eq. 1:

$$y = [M_1(1-u_1) - M_0(1-u_0)] / V \qquad (1)$$

where: y is the drug dosage (kg·m^{-3}), M_0 is the specimen mass before treatment (kg), u_0 is the moisture content of bamboo strips specimen before treatment (%), M_1 is the specimen mass after treatment (kg), u_1 is the moisture content of bamboo strips specimen after treatment (%), and V is the specimen volume before treatment (m^3).

Hygroscopicity

Hygroscopicity of bamboo strips specimen was determined according to ASTM D3201/ D3201M (2013). Specimens (100 × 20 × 5 mm) were treated in a humidity box at 27 ± 2°C, 90 ± 3% RH for 168 h according to ASTM D3201/D3201M (2013). After that, the moisture absorption of treated specimen was calculated according to Eq. 2:

$$w = (M_3 - M_2) / M_2 \times 100\% \qquad (2)$$

where: w is moisture absorption (%), M_2 is the specimen mass before hygroscopic testing (kg), and M_3 is the specimen mass after hygroscopic testing (kg).

Leaching resistance

Leaching test was performed according to AWPA E11 (AWPA 2006) standard. Treated bamboo strips specimens (100 × 20 × 5 mm) were impregnated in deionized water for 14 days. Deionized water was changed after 6 h, 24 h and 48 h, and thereafter at 48 h intervals. When leaching test finished, samples were left for 1 d at room temperature before oven drying for 12 h at 60°C and 12 h at 103 ± 2°C to achieve a constant weight (AWPA 2006). The leaching resistance value (LRV) of treated samples was calculated according to Eq. 3:

$$l = (y_2 / y_1) \times 100\% \qquad (3)$$

where: l is the LRV (%), y_1 and y_2 are the drug dosage of treated specimen before and after extraction respectively ($kg \cdot m^{-3}$).

Microstructure observation

To determine the distribution of fire retardant in the bamboo strips, small samples with dimension of 10 × 5 × 1.5 mm (L × W × T) were cut from the transverse section of treated and untreated bamboo strips. Before observed by a scanning electron microscope (SEM, SS-550, Shimadzu, Kyoto, Japan) at an accelerating voltage of 5 kV, each sample surface should be sputter-coated with a thin layer of gold.

Energy dispersive X-ray spectroscopy (EDX) analysis

To study the changes in the amount of fire retardant elements before and after leaching test of treated bamboo strips, small samples with dimension of 10 × 10 × 5 mm (L × W × T) were cut from the two ends of treated bamboo strips. FESEM (SIRION-100, FEI, Hillsboro, USA) equipped with EDX (Genesis 4000, AMETEK, California, USA) was used to measure the change in elemental content with an accelerating voltage of 25 kV.

Thermogravimetric (TG) analysis

To analysis the thermal stability of treated and untreated bamboo strips, TG data of each specimen was obtained from a TG 209 F1 thermal analyzer. Each sample was processed into powder of about 8 mg, and then samples were displaced into a sintered-alumina crucible and heated at the rate of $10°C \cdot min^{-1}$ from ambient temperature to 800°C. The flow of dynamic carrier nitrogen gas was set at a rate of $40\ mL \cdot min^{-1}$.

Fourier-transform infrared spectrometer (FTIR) analysis

To study the change of chemical bonds and the combination mode between functional components and bamboo strips, the method of tableting with KBr was used in FTIR (Nicolet 6700) test. The powder of treated and untreated specimen was oven-dried, and then the KBr was dried at 200°C in a muffle oven for 24 h. After that, testing samples were obtained by mixing about 1-2 mg oven dried samples with 100–200 mg KBr. The FTIR curves of samples were obtained at the test scanning range of 4000-400 cm^{-1}.

RESULTS AND DISCUSSION

Moisture absorption and leaching resistance

The mass of fire-retardant in treated materials will decrease due to the absorption and extraction of water, which means the loss of fire-retardant can lead to degradation of fire retardant properties of treated materials. Thus, we use moisture absorption rate and leaching resistance value (LRV) to evaluate the hygroscopicity (moisture absorption) and leaching resistant performance of fire-retardant bamboo materials. The lower the moisture absorption rate, the higher the LRV, the better the performance of fire-retardant bamboo strips. The moisture absorption rate and LRV of treated and untreated bamboo strips are shown in Tab. 1.

It can be seen from Tab. 1 that under the condition of similar drug dosage, the hygroscopicity of the treated bamboo specimen was significantly higher than that of untreated one. That means the hygroscopicity of water-based fire retardant is higher than that of bamboo itself. And the hygroscopicity of bamboo strips treated with compound fire retardant containing BA is significantly lower than that of containing DOT, which indicates that the hygroscopicity of DOT is significantly higher than BA.

Tab. 1: Moisture absorption rate and LRV of fire-retardant and non-fire-retardant bamboo strips.

Samples	Drug dosage (%)	Moisture absorption rate (%)	Leaching resistance value (%)
AD	2.8	9.5	35.5
ADS	3.1	9.0	52.3
AB	2.8	7.8	22.9
ABS	3.1	8.0	83.2
Control	0	7.5	-

In addition, under the condition of similar drug dosage, the comparison results of the hygroscopicity of bamboo strips treated with four compound fire retardants is: AB<ABS<ADS<AD, and the comparison of the LRV is: AB<AD<ADS<ABS. So, the addition of nano-SiO_2 sol can reduce the hygroscopicity and improve the leaching resistance of bamboo strips treated with compound fire retardant significantly. This effect may due to good permeability of nano-SiO_2 sol, which means it can penetrate into the basic tissue parenchyma cells of bamboo, fill the cell gap of bamboo, reduce the water seepage channel, and decrease the hygroscopicity of bamboo. Furthermore, nano-SiO_2 sol has a micelle diameter of 10 to 100 nm, which means it has strong adsorption capacity and a large specific surface area, so it can encapsulate and adsorb the nitrogen-phosphorus-boron compound fire retardant inside the bamboo strips. Moreover, the SS dried and solidified into a silica gel after entering the bamboo strips, it can combine with the free hydroxyl groups in the cellulose molecular chain by hydrogen bonding of its unreacted hydroxyl groups. And then, the hydroxyl group on the cell wall is condensed with the silanol produced by the hydrolysis of the precursor, the treated material and the silica are connected by Si-O-C bond, thereby connecting the inorganic molecule to the cellulose macromolecular chain in the cell wall. In addition, the silica gel itself has good hydrophobicity, which hinders the absorption of moisture by the bamboo, thereby reducing or slowing the rate of migration of the nitrogen-phosphorus-boron compound fire retardant from the bamboo strips. Overall, bamboo treated with ABS has the lowest hygroscopicity and the best leaching resistance performance.

SEM analysis

Fig. 1 shows the SEM images of fire-retardant and non-fire-retardant bamboo strips. Fire-retardant bamboo strips means bamboo strips impregnated with compound fire retardants (AD, AB, ADS and ABS). Correspondingly, non-fire-retardant bamboo strips refer to untreated bamboo strips. Compared with non-fire-retardant bamboo strips (Fig. 1a), the Figs. 1b-e show that the internal structure has not changed in fire-retardant bamboo strips.

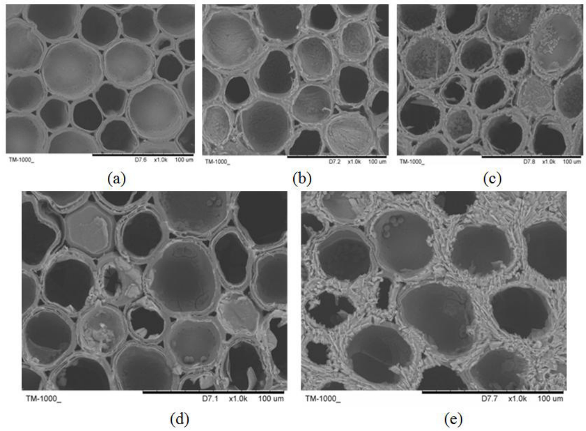

Fig. 1: *SEM images of fire-retardant and non-fire-retardant bamboo strips: (a) control,(b) AD, (c) AB, (d) ADS, (e) ABS.*

As is shown above, fire retardant AD and AB are in the form of rods and granules, respectively, and are physically filled in cell cavity and cell gap of bamboo. Compared with Fig. 1a, Fig. 1d and Fig. 1e show that compared with the non-fire-retardant bamboo strips, after fire-retardant treatment, the thin-walled cells and ducts of bamboo sheet basically maintain original microstructure. It can be seen from Fig. 1d that the nano-SiO_2 sol in the compound fire retardant ADS was dried and solidified in cell cavity of bamboo parenchyma cells to form a dense SiO_2 gel layer, which plays a role in encapsulation and adsorption effect on the nitrogen-phosphorus-boron compound fire retardant entering the cell cavity of bamboo, which means it can slow down the rate of migration of compound fire retardant from bamboo to some extent. In addition, it can be seen from Fig. 1e that the nano-SiO_2 sol in compound fire retardant ABS not only penetrates into cell cavity of bamboo to form a dense SiO_2 gel layer, which can encapsulates and adsorbs the nitrogen-phosphorus-boron compound fire retardant entering the cell cavity; but also penetrates into the intercellular space between thin-walled cells of bamboo, forming SiO_2 gel crystals, which can hinder the absorption of moisture by the bamboo and slow the rate of migration of compound fire retardant from bamboo more effectively.

EDX Analysis

Fig. 2 shows the elemental analysis image of bamboo strips treated by compound fire retardant AD before and after leaching test.

According to the elemental content data of bamboo treated with AD, before the leaching test, the weight percentage of Na and P elements in the bamboo treated with AD are 2.3% and 4.4%, respectively, and the atomic percentage are 1.4% and 2.0%, respectively. That means fire-retardant AD enters the inside of bamboo, but P and Na elements are all lost after leaching test, which means the leaching resistance of AD is poor.

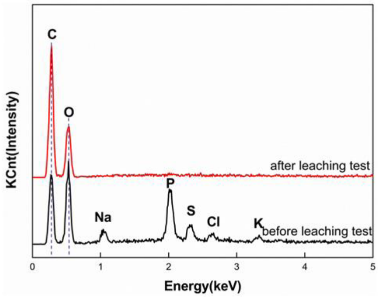

Fig. 2: Elemental analysis image of bamboo strips treated by compound fire retardant AD.

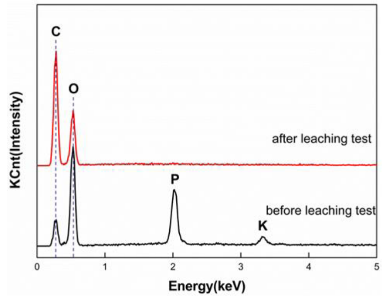

Fig. 3: Elemental analysis image of bamboo strips treated by compound fire retardant AB.

Fig. 3 shows the elemental analysis image of bamboo strips treated by compound fire retardant AB before and after leaching test. According to the elemental content data of bamboo treated with AB, before the leaching test, the weight percentage of P in the bamboo treated with AB is 7.7% and the atomic percentage is 3.8%. That is to say, fire-retardant AB enters the inside of bamboo, but the element of P is all lost after the leaching test, which means the leaching resistance of AB is also poor.

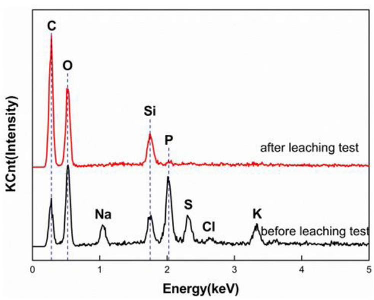

Fig. 4: Elemental analysis image of bamboo strips treated by compound fire retardant ADS.

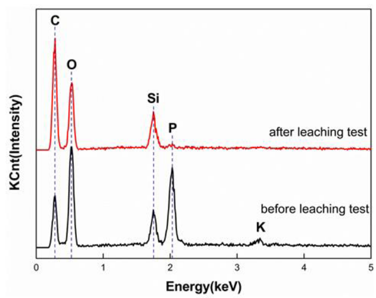

Fig. 5: Elemental analysis image of bamboo strips treated by compound fire retardant ABS.

Fig. 4 shows the elemental analysis image of bamboo strips treated by compound fire retardant ADS before and after leaching test. According to the elemental content data of bamboo treated with ADS, before the leaching test, the weight percentage of the Na, Si and P elements in the bamboo treated with ADS are 3.9%, 2.5% and 5.9%, respectively, and the atomic percentages are 2.5%, 1.3% and 2.9%, respectively. That is to say, fire-retardant ADS enters the inside of bamboo. The Na element is completely lost, the P element has a small amount remaining, and the loss of Si element is small, which indicates that the addition of the nano-SiO_2 sol can effectively enhance the leaching resistance of the bamboo treated with compound fire retardant ADS.

Fig. 5 shows the elemental analysis image of bamboo strips treated by compound fire retardant ABS before and after leaching test. According to the elemental content data of bamboo treated with ABS, before the leaching test, the weight percentages of the Si and P elements in the bamboo treated with ABS are 2.6% and 6.3%, respectively, and the atomic percentage are 1.3% and 3.0%, respectively. That is to say, fire-retardant ABS enters the inside of bamboo.

The P element has some remaining, and the loss of Si element is small, which indicates that the addition of the nano-SiO_2 sol can effectively enhance the leaching resistance of the bamboo treated with compound fire retardant ABS.

TG Analysis

According to the results of hygroscopicity, leaching resistance, SEM and EDX analysis, we found fire-retardant AB and ABS have better performance than AD and ADS, so we only used TG and FT-IR to test AB and ABS except untreated bamboo strips. Fig. 6 and Fig. 7 show the TG and DTG curves of bamboo strips treated by compound fire retardant AB and ABS respectively.

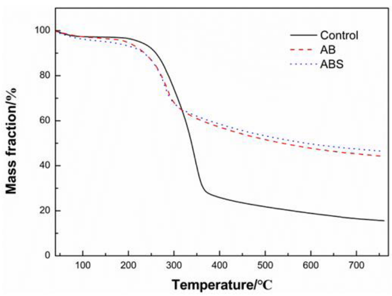

Fig. 6: TG curves of fire-retardant and non-fire-retardant bamboo strips.

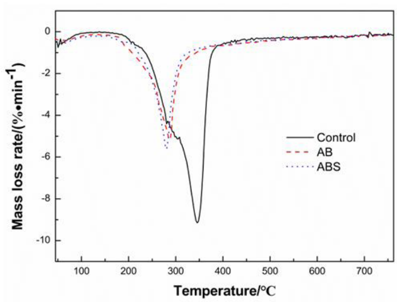

Fig. 7: DTG curves of fire-retardant and non-fire-retardant bamboo strips.

Tab. 2 shows thermal analysis parameters of fire-retardant and non-fire-retardant bamboo strips. Fire-retardant bamboo strips means bamboo strips impregnated with compound fire retardants AB and ABS. Correspondingly, non-fire-retardant bamboo strips refer to untreated bamboo strips.

Tab. 2: Thermal analysis parameters of fire-retardant and non-fire-retardant bamboo strips.

Sample	Wd/%	T1/°C	Wc/%	Mc/%	M500/%	M700/%
Control	2.65	345	65.18	31.88	21.79	16.50
AB	3.27	287	36.40	60.11	51.61	45.29
ABS	4.45	279	33.87	61.19	53.29	47.45

Fig. 6 and Fig. 7 show the thermogravimetric (TG) and derivative thermogravimetry (DTG) curves of fire-retardant and non-fire-retardant bamboo strips. Tab. 2 shows the weight loss W_d in the dehydration stage, the weight loss *Wc* in the carbonization stage, the peak temperature T_1 in the carbonization stage of the bamboo, the carbonization residual *Mc*, the residual weight M_{500} at 500°C, and the residual weight M_{700} at 700°C from the TG and DTG curves of the fire-retardant and non-fire-retardant bamboo strips.

It can be seen from Figs. 6, 7 and Tab. 2 that the thermal degradation performance of bamboo has undergone some changes. As the temperature rises, the rate of pyrolysis weight loss of bamboo increases first and then decreases. The pyrolysis of fire-retardant and non-fire-retardant bamboo has mainly gone through three stages. The first stage (40°C ~150°C) is the dehydration stage (mainly the evaporation process of water), the weight loss rate of fire-retardant and non-fire-retardant bamboo is about 2.5~4.5%, and the fire-retardant bamboo loses weight before the untreated one. It may be due to the polycondensation of ammonium phosphate in the compound fire retardant to produce a strong acid, which has the function of catalytic dehydration. The second stage occurs in the range of 150°C ~360°C, which is the carbonization stage (mainly the decomposition of hemicellulose, lignin and cellulose). In this stage, the weight loss of non-fire-retardant bamboo is 65.2%, while the weight loss of bamboo treated with ABS and AB are just 33.9% and 36.4%. That is to say, the ammonium dihydrogen phosphate (ADP) in the compound fire retardant can not only promote the dehydration of bamboo into charcoal, reduce the initial decomposition temperature of bamboo, make the reaction termination temperature advance, but also generate non-flammable pyrolysis gas, which can dilute combustible gas to achieve the effect of fire retardant (Jin et al. 2015). In addition, the boric acid (BA) in the compound fire retardant can form a protective layer of the glassy residue on the surface of the treated bamboo (Tomak et al. 2012), thereby effectively preventing further volatilization of the treated bamboo strips and accelerating the carbonization of the bamboo material.

Figs. 6 and 7 show that the peak of mass loss rate of bamboo treated with AB and ABS are 58°C and 66°C earlier than untreated bamboo. Moreover, the width of the peak is narrowed, and the range of main pyrolysis stage is reduced, which means after the fire retardant treatment, the flaming burning time of bamboo is shortened, and actually, the fire time can be shortened, the risk of fire is reduced, and the fire retarding effect is achieved (Jin et al. 2015). The third stage occurs after 360°C, which is the calcination stage. At this time, the weight loss rate of the fire-retardant and non-fire-retardant bamboo materials gradually slows down (mainly the flameless combustion of the carbon residue). It can also be seen from Fig. 6 that the residual mass fraction of pyrolysis of the untreated bamboo is 16.5% at 700°C, and the residual mass fraction of bamboo treated with AB and ABS is 45.3% and 47.6% respectively, which is nearly double that of the non-fire-retardant bamboo strips. This indicates that the addition of the compound fire retardant is beneficial to strengthen the char forming effect of the bamboo, and correspondingly increases the amount of carbon, which can suppress the combustion better. Furthermore, compared with compound fire-retardant AB, the initial decomposition temperature and the maximum weight loss rate of bamboo treated with compound fire-retardant ABS are lower, and the residual mass fraction at 700°C is higher, which indicate that bamboo treated with ABS has a better thermal stability than AB.

FT-IR Analysis

Fig. 8 shows the FT-IR image of fire-retardant and non-fire-retardant bamboo strips. It can be seen from Fig. 8 that most characteristic peaks of untreated bamboo are similar to bamboo treated with AB and ABS, which means that the compound fire retardant is mainly filled in the bamboo material by physical combination, and does not change the basic structure and properties of the bamboo. Fig. 8 also shows that the FT-IR image of bamboo treated with AB and ABS has an absorption band generated by P=O stretching vibration at 1250-1253 cm^{-1}, (Zhu et al. 2014) which means that ADP has entered the interior of the bamboo.

In the vicinity of wave number of 1000 cm^{-1}, the characteristic peaks produced by the stretching vibration of cellulose primary alcohol C-O can be seen in the fire-retardant and non-fire-retardant bamboo strips. But the peak wave shape of the fire-retardant bamboo is wider and blunter than that of the untreated bamboo, and the peak wave shape of the bamboo treated with ABS is more wide and blunt. That is to say, both AB and ABS are associated with primary hydroxyl group of the bamboo cellulose, and the bamboo treated with ABS is more strongly associated with free primary hydroxyl group.

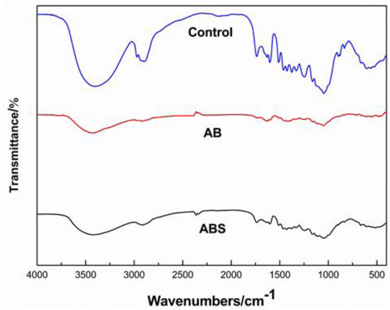

Fig. 8: FT-IR image of fire-retardant and non-fire-retardant bamboo strips.

In addition, the FT-IR image of bamboo treated with ABS shows that at wave numbers of 1080-1110 cm^{-1} and 450-460 cm^{-1}, characteristic peaks due to linear asymmetric stretching and bending vibration of Si-O-Si can be seen clearly (Kioul and Mascia 1994, Mo et al. 2007). And at 1020-1040 cm^{-1}, we can see the absorption band produced by the Si-OH group (Cornelius and Marand 2002), which means that the fire-retardant bamboo contains nano-SiO_2 sol. Furthermore, although the FT-IR image of treated and untreated bamboo both have characteristic peaks generated by O-H stretching vibration at 3000-3500 cm^{-1}, the peak wave shape of bamboo treated with AB and ABS are smaller and wider than that of untreated bamboo, and the peak shape of bamboo treated with ABS is more small and wide, which indicates that both AB and ABS are associated with the free hydroxyl groups of the bamboo cellulose, and ABS has a more strongly association with the free hydroxyl groups.

CONCLUSIONS

(1) Compared with AD, ADS and AB, bamboo strips treated with ABS (ammonium dihydrogen phosphate + boric acid + nano-SiO_2 sol) have lower hygroscopicity (8.0%) and the best leaching resistance performance (83.2%). (2) EDX analysis result shows that compared with other three compound fire retardants (AD, ADS, and AB), the leaching resistance capability of bamboo strips treated with ABS has the most improvement, which can be seen from weight percentages and atomic percentages of the Si and P elements before and after the leaching test. (3) Compared with non-fire-retardant bamboo strips, the thermal stability of bamboo strips treated with AB and ABS has obviously improved, which can be seen from the improvement in the residue weight M700 from 16.5% to 45.3% and 47.5%. In addition, the FTIR analysis can also support this improvement. (4) Therefore, the optimum compound fire retardant for bamboo to impregnate is ABS.

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REFERENCES

1. Altun, S., Ozcifci, A., Senel, A., 2010: Effects of silica gel on leaching resistance and thermal properties of impregnated wood. Wood Research 55(4): 101-112.
2. Cornelius, C.J., Marand, E., 2002: Hybrid inorganic–organic materials based on a 6FDA–6FpDA–DABA polyimide and silica: physical characterization studies. Polymer 43(8): 2385-2400.
3. Chu, D., Mu, J., Zhang, L., 2017: Promotion effect of NP fire retardant pre-treatment on heat-treated poplar wood. Part 2: hygroscopicity, leaching resistance, and thermal stability. Holzforschung 71(3): 217-223.
4. Du, C.G., Wei, J.G., Jin, C.D., 2016: Fire retardant treatment process of bamboo scrimber. Journal of Forestry Engineering 1(1): 51-54.
5. Du, C.G., Shu, T.T., Ye, B.B., 2010: Study on permeability characteristics of dye solution in bamboo strip and its influence factors. Journal of Zhejiang Forestry Science and Technology 30(5): 9-13.
6. Jin, X.B., Li, Y.Y., Wen, X.W., 2015 : The thermal degradation and combustion properties of bamboo treated with P-N-B flame retardant. China Forest Products Industry 42(12): 40-44.
7. Kartal, S.N., Hwang, W.J., Imamura, Y., 2007: Water absorption of boron-treated and heat-modified wood. Journal of Wood Science 53(5): 454-457.
8. Kioul, A., Mascia, L., 1994: Compatibility of polyimide-silicate ceramers induced by alkoxysilane silane coupling agents. Journal of non-crystalline solids 175(2-3): 169-186.
9. Li, C.Y., Lv, C.Y., Yu, L.L., 2019: Flame retardant treatment of bamboo and its effect on bamboo properties. World Bamboo and Rattan 17(6): 16-20, 24.
10. Li, N., Chen, Y.H., Weng, F.J., 2017: The performance comparison of 5 kinds of bamboo fire retardants. Journal of Bamboo Research 36(3): 62-65.
11. Li, Y.J., Xu, B., Zhang, Q.S., Jiang, S.X., 2016a: Present situation and the countermeasure analysis of bamboo timber processing industry in china. Journal of Forestry Engineering 1(1): 2-7.
12. Li, Z., De-Miao, C., Xue-Tong, S., 2016b: Effect of silane coupling agent on waterproof and flame retardant properties of poplar wood treated with flame retardant. Bulletin of the Chinese Ceramic Society 35(01):19-24.
13. Lou, C.C., Qian, X.Q., Lai, J.Y., 2010: Study on fire retardant treatment of Chinese fir by nano-SiO_2 sol . Low Temperature Architecture Technology 32(05):4-5.
14. Mo, T.C., Wang, H.W., Chen, S.Y., 2007: Synthesis and characterization of polyimide–silica nanocomposites using novel fluorine-modified silica nanoparticles. Journal of applied polymer science 104(2): 882-890.
15. Na, B., Yue, K., Lu, X.N., Yin, W.P., 2009: Study on retard leach resistant of modified fast-grown poplar. Journal of Nanjing Forestry University (Natural Sciences Edition) 33(1): 25-29.
16. Pan, J., Mu, J., Wu, Z., Zhang, X., 2014: Effect of nitrogen-phosphorus fire retardant blended with Mg(OH)2/Al(OH)3 and nano-SiO_2 on fire-retardant behaviour and hygroscopicity of poplar. Fire and Materials 38(8): 817-826.
17. Son, D.W., Kang, M.R., Kim, J.I., Park, S.B., 2012: Fire performance of the wood treated with inorganic fire retardants. Journal of the Korean Wood Science and Technology 40(5): 335-342.

18. Tomak, E.D., Baysal, E., Peker, H., 2012: The effect of some wood preservatives on the thermal degradation of Scots pine. Thermochimica Acta 547(547): 76-82.
19. Xue, S.Q., Li, B., Feng, K.X., 2006: Characteristics and application of water-based fire retardants. Fire Technique and Products Information (8): 25-27.
20. Yao, X.L., Peng, R., Du, C.G., 2019: A two-step method for fabricating bamboo culm coated with MgAl-LDHs and its fire resistance properties. BioResources 14(3): 5150-5161.
21. Zhang, X., Li, D., Xie, H., Wang, D., 2014: Preparation and application of water-based fire retardant of ammonium phosphate. Advanced Materials Research 1015: 287-290.
22. Zhang, X.T., Mu, J., Chu, D.M., Zhao, Y., 2015: Synthesis of fire retardants based on N and P and poly(sodium silicate-aluminum dihydrogen phosphate) (PSADP) and testing the flame-retardant properties of PSADP impregnated poplar wood, Holzforschung 70(4): 341-350.
23. Zhang, X.T., Mu, J., Chu, D.M., Zhao, Y., 2016: A study on the fire performance and hygroscopicity of poplar treated with melamine modified N-P fire retardant. Journal of Central South University of Forestry & Technology 36(2): 119-124.
24. Zheng, M.H., Wang, K., Wu, Q., 2016: The performances of bamboo treated with three flame retardants. Journal of Bamboo Research 35(4): 8-13.
25. Zhou, Z.X., Yao, X.L., Du, C.G., 2018: Effect of hygroskopicity of fire retardant on hygroscopicity of fire retardant bamboo chips. Wood Research 63(3): 373-382.
26. Zhu, X., Wu, Y., Tian, C., 2014: Synergistic effect of nanosilica aerogel with phosphorus flame retardants on improving flame retardancy and leaching resistance of wood. Journal of Nanomaterials 2014: Article ID 867106.

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