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ADSORPTION AND FIXATION OF SOLUBLE FIRE RETARDANCY IN *POPULUS RUSSKII* AND *CUNNINGHAMIA LANCEOLATA*

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ABSTRACT

Flame retardant treatment is a common method of wood preservation. However, the factory usually uses the same approach to all the wood, but lack of targeted so as to cause waste. This study used poplar and Chinese fir as the species investigated. These species were dipped with boron-nitrogen-phosphorus (B-P) fire retardant. The influences on material loading of processing method, concentration of fire retardant, and drying method were investigated. The contents of B and P were tested by inductively coupled plasma optical emission spectrometry (ICP-OES), after distilled water washing and ultrasonic washing. The results showed that the volume loading increased with the concentration of fire retardant. Freeze-drying can noticeably improve the volume loading, and the impact of the drying method was more notable on poplar than on Chinese fir. The fixation effect of the B and P in poplar was lower by ultrasonic washing than that was by distilled water washing. The fixation effect was opposite in the Chinese fir. Vacuum process was more suitable for the poplar (hardwood), and vacuum-pressure process was more suitable for the Chinese fir (soft wood).

KEYWORDS: Fire retardant, adsorption, fixation.

INTRODUCTION

Flame retardant treatment is a conventional method of wood preservation. Flame retardant wood possesses many positive characteristics, such as a low burning rate, slow flame propagation velocity, and a fast carbonization process of the burning surface (He et al. 2012). Flame retardant wood is an excellent material used in the fields of construction and decoration. Fire retardancy has been widely researched to improve the fire safety of wood and achieved some results (Taghiyari 2012; Pan and Song 2012; Wang et al. 2014; Shen et al. 2008; Saka and Tanno 1996; Getto and

Ishihara 1998; Zhang et al. 2015). Boron has a low mammalian toxicity but remarkable plant toxicity, and is effective as an insecticide and fungicide (Yalinkilic 1999). The complementary and synergistic effect between the elements make the flame retardant system has the multiple effects such as flame retardant, anticorrosion, insect prevention and antimildew.

Wood fire retardant effect is not only related with the type of flame retardant, but also related with the adsorption and fixation of flame retardant in wood. The key is how to improve the adsorption and fixing performance of flame retardant. Thevenon et al. (1997) found a combination of tannins and boric acid was presented as beneficial. Toussaint-Davergne et al. (2000) presented a system based on glycerol/glyoxal and boric acid mixtures intended for hazard class III. Lesar et al. (2009) studied the effects of fungicide (boric acid, borax) concentration on the adsorption properties of wood, finding that the dipping treatment impacted the wood equilibrium moisture content less in the case of relatively low air humidity. Ramos et al. (2006) researched the thermodynamics and kinetics of the adsorption of boron and boron compounds in pine, finding that although the reaction rate between boric acid and polysaccharides was faster than with lignin, the reaction speed was very slow at temperatures below 20°C. Thus, boron preservatives easily eluted in the wood.

In the current industry method, flame retardant wood is usually treated by vacuum-pressure method. However, different wood has different pore characteristics, so the permeability and adsorption characteristics of the flame retardant are also different. The production costs will increase if there has not the targeted processing methods. In this paper, the adsorption properties of the flame retardant in different tree species and different drying methods were studied under different impregnation methods. The research will provide the theoretical basis for the actual production, and reduce the cost of production.

MATERIAL AND METHODS

Twenty-year-old *Populus russkii* (poplar) was obtained from the Wulumuqi region of Xinjiang Province. Fifteen-year-old *Cunninghamia lanceolata* (Chinese fir) was obtained from the Guangzhou region of Guangdong Province. The moisture content of the wood was adjusted from 80% to 12% via conventional drying methods. Specimens with dimensions of 20 (L) × 20 (T) × 20 (R) mm were sawn for the next experiments. The density of poplar was 0.45 $g \cdot cm^{-3}$, and the density of Chinese fir was 0.33 $g \cdot cm^{-3}$.

Boron (B) and phosphorus (P) fire retardant was derived from the market. Boron as the main agent, compound phosphorus, nitrogen and other components. Diboron trioxide content is greater than 50%. It was the white crystal and dissolved into the required concentration when used.

Methods

Fire-retardant treatment

Samples were dipped using normal pressure process impregnation, vacuum process impregnation and vacuum-pressure process impregnation. Five samples were selected randomly for each experiment. In the normal pressure impregnation experiment (at 20°C), concentration was the main study object. Samples were completely dipped in 600 mL of the fire retardant, the mass concentration of which was either 5 %, 10 %, 15 %, and 20 %. A glass block was placed above the samples to prevent them from floating. The beaker was sealed by a plastic film to prevent volatilization and then placed 12 h under atmospheric conditions.

In the vacuum process impregnation experiments (at 20°C), samples were put in the beaker (1000 mL), and then the beaker was placed in a desiccator (11L). One end of the dryer was connected with a vacuum pump and the other was a switching device. Fist, the switch was closed and the vacuum pump was vacuumed to -0.1 MPa keeping 30 min. Then the switch was opened and the 600 mL of the fire retardant (the concentration of which was either 5 %, 10 %, 15 %, or 20 %) was inhaled in the beaker with releasing the vacuum. The beaker was sealed by a plastic film and then placed 2 h under atmospheric conditions.

In the vacuum-pressure process impregnation experiment (at 20°C), specimens were kept 30 min in a vacuum of -0.09 MPa, then were applied pressure of 0.8 MPa and hold on 2 h. The concentration of the flam retardant was 15%.

Fire-retardant treatment with various drying methods

Five dry samples from each drying type (air drying, conventional drying, and freeze-drying) were dipped by normal pressure process and vacuum process impregnation methods respectively. The concentration of the fire retardant was 15 %. The moisture content of the air-drying sample was 12 %. Freeze-drying samples were frozen for 24 h in the pre-freeze chamber of a vacuum freezing dryer (Shuangjia Corp., China) and then were dried for 46 h at a condensation temperature of -50 °C under -16.5 Pa vacuum.

The volume loading (R) were calculated using Eq. 1

$$R = [(W_2 - W_1) \times C / V]/10^{-5} \quad (1)$$

where: R is the volume loading ($kg \cdot m^{-3}$),
W_2 - the mass after dipping (g),
W_1 - the mass of the sample,
C - the mass percentage concentration of the fire retardant (%),
V - the volume of the sample (mm^3).

Fixation of the fire retardant

Vacuum impregnation samples were washed respectively by distilled water immersion and ultrasonic oscillations. In the distilled water immersion washing, flame retardant wood were dipped in 200 mL water for 10 h, and the water (at 20°C) was replaced once every 2h. In the ultrasonic oscillation washing, flame retardant wood samples were dipped in a beaker with 200 mL of water that was then placed in an ultrasonic vibration box (ultrasonic power, 200 W; ultrasonic frequency, 40 KHz; Kunshan Corp., China) for 30 min. After the experiment, the samples were wiped dry and placed indoors for 7 days (at 20°C and 75 % relative humidity). The air-drying specimens were crushed to 80-mesh and digested by nitric and perchloric acids. Then, the contents of B and P were tested by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Corp., USA). The specific digestion methods were as follows: wood flour (0.25 g) was dried in an oven at 103°C and then placed in a quartz tube, to which 2.5 mL of nitric acid was added. The tube was placed in the digestion instrument at 150°C for 1 h and 2 mL of perchloric acid was added to the tube. The temperature was increased to 180°C and maintained until the solution was clear and transparent. The digestion solution was diluted to 1000 mL with deionized water.

To understand the adsorption and fixation of flame retardant in wood, specimens were examined by Scanning electron microscope (SEM, XL-30-ESEM, FEI, Holland).

RESULTS AND DISCUSSION

Volume loading of fire-retardant

Fig. 1 shows that in the normal pressure impregnation, the volume loading of Chinese fir was higher than poplar by 43.8 %, 15.1 %, 25.4 %, and 44.5 % when the solution concentrations were 5 %, 10 %, 15 %, and 20 %, respectively. In general, the surface free energy of poplar is higher than that of Chinese fir (Bao et al. 2004). And the porosity of Chinese fir is bigger than poplar. Therefore, when there is no other external influence, the adsorption of aqueous solution on Chinese fir is greater than on poplar. However, the material loading of poplar was better than that of Chinese fir when the vacuum impregnation process was used. The permeability of poplar (hardwood) is better than that of Chinese fir (softwood) (Bao and Lv 1992), and the exclusion of air in the wood by the pre-vacuum process was contribute to the impregnation of fire retardant. But the pressure is not enough to make the fire retardant entering the smaller pores. In the vacuum-pressure process impregnation, the volume loading of poplar was higher than that of the Chinese fir. The fire retardant particles could enter into the cell gap and pit under the pressure, so the increasing of volume loading was obviously.

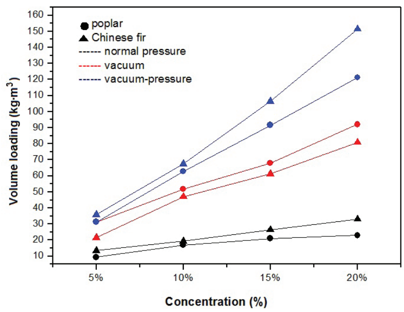
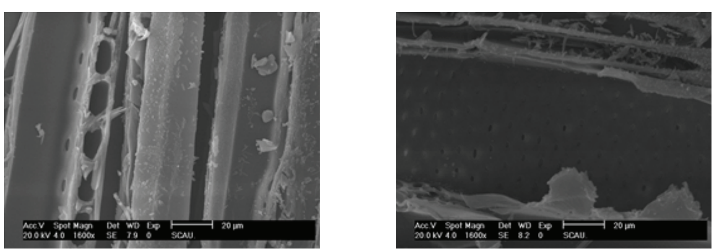


Fig. 1: Effect of concentration on volume loading.

Poplar have big vessel and vessel perforation (20-400μm). The permeability of poplar will increase notable due to the reduction of gas in the vessel by vacuum. The bordered pits of Chinese fir is about 400 nm ~ 6μm (Butterfield 2006), but the pits of poplar was smaller than that of Chinese fir as showed in Fig. 2. The average particle size of flame retardant was 786.6 nm (examined by Laser particle size analyzer, Mastersizer 3000, Malvern, UK). So some pits of poplar were blocked under certain pressure as showed in figure 2 (b). Meanwhile, the density of Chinese fir specimens is lower than that of poplar, so the porosity of Chinese fir is greater than that of poplar. So the flam retardant would enter the wood porosity easily under a certain pressure.



a: Chinese fir *b: Poplar*

Fig. 2: SEM of impregnated wood

Effect of drying method on volume loading

The poplar and Chinese fir samples were dried by air drying, conventional drying, and freeze-drying, then were dipped by normal pressure and vacuum method respectively. The following conclusions were obtained.

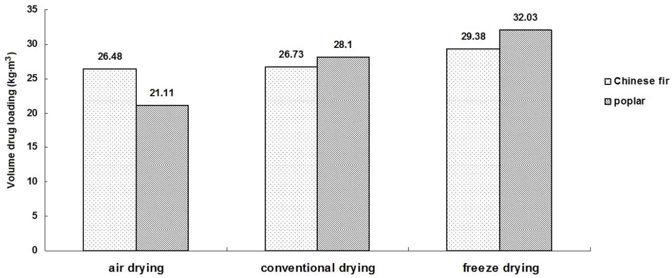


Fig. 3: Volume loading of different drying methods—normal pressure process.

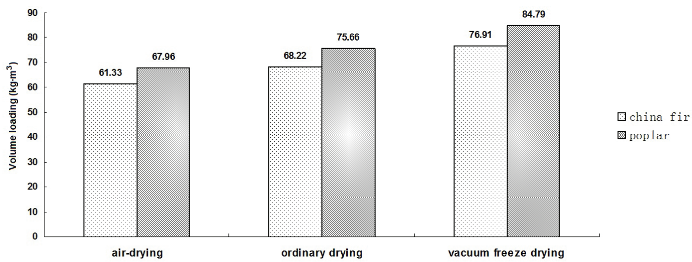


Fig. 4: Volume loading of different drying methods— vacuum process.

Figs. 3 and 4 shows that the volume loading increased noticeably after freeze-drying. In the normal pressure impregnation process, the volume loading of freeze dried Chinese fir samples were 11.0% and 9.9% higher than that of air dried and conventionally dried samples, respectively. The volume loading of freeze dried poplar samples were 51.7% and 14.0% higher than that of air dried and conventionally dried samples, respectively (Fig. 3). In the vacuum impregnation process, the volume loading of freeze dried Chinese fir samples were 25.4% and 12.7% higher than that of air dried and conventionally dried samples, respectively. The volume loading of freeze dried poplar samples were 24.7% and 12.1% higher than that of air dried and conventionally dried samples, respectively (Fig. 4). Freeze-drying is a special method which water in the wood is frozen into ice at low temperatures and the solid water is sublimated directly to dryness (Butterfield 2006). Some pits membrane were cracked obviously, as showed in Fig. 5. This could be considered as amplifying the effective radius of pit membrane pores, so the permeability of the volume loading of freeze dried samples increased noticeably. (Lu 2005).

The influence of drying method of poplar on the volume loading was more obvious than that of Chinese fir, especially in the normal pressure process. Because the fluid of softwood circulates through pits in tracheids. However, in hardwood, the fluid circulates not only through pits, but also through the perforation at the end of pores (Siau 1984). The number of permeable effective capillary of poplar is much more than that of Chinese fir, so the permeability increases with the decrease of water content (Bao et al. 1984).

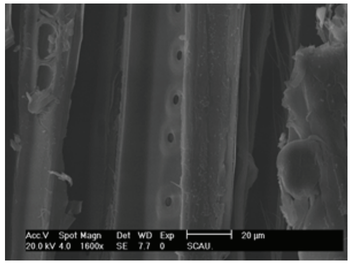


Fig. 5: crack of pit membrane by freeze drying.

Anchor effect of fire retardants

The air dried samples were dipped by the vacuum process, and then were washed by distilled water and ultrasonically respectively. The contents of B and P were tested by ICP-OES.

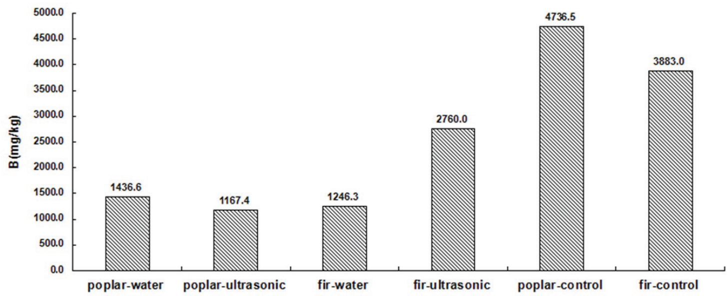


Fig. 6: The content of boron

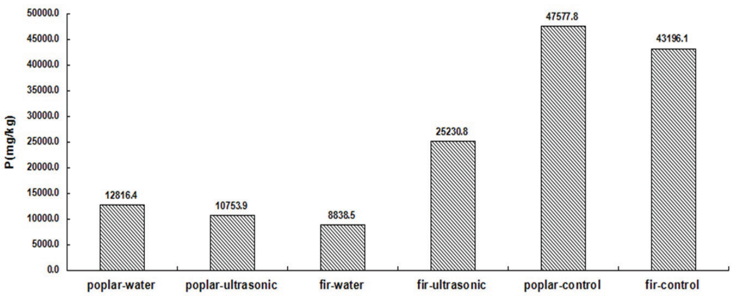


Fig. 7: The content of phosphorus.

Figs. 6 and 7 shows that the contents of B and P in the poplar were higher than those in the Chinese fir. The main effective components (B and P) were noticeably decreased by distilled water and ultrasonic washing. The decrease of the B and P contents of poplar were more pronounced than that of Chinese fir. After distilled water washing, the contents of B and P in air dried poplar decreased by 69.7% and 73.1%, respectively, whereas those in the Chinese fir decreased by 67.9% and 79.5%, respectively. After ultrasonic washing, the contents of B and P in the air dried poplar decreased by 75.4% and 77.4%, respectively, whereas those in the Chinese fir decreased by 28.9% and 41.6%, respectively. In Chinese fir, the decrease of the B and P contents by distilled water washing was markedly higher than by ultrasonic washing. In poplar, the effect of two methods was matched because the liquid in the wood generated cavitation such that some solute particles could rapidly break away from the wood. Liquid in Poplar (hardwood) transmits through perforations which is at the end of wood pores. The ultrasonic effect can facilitate the movement of solute particles to a certain extent. Thus, the contents of B and P were noticeably decreased by both distilled water and ultrasonic washing. However, in the Chinese fir (softwood), the liquid transmittance primarily depended on the pits (with diameters of approximately 3 to 8 μm) of the tracheid. Particulate matter inside the wood was accelerated by ultrasonic washing, resulting in the blockage of pits. Therefore, the decrease in the B and P contents in Chinese fir by ultrasonic washing was lower than that caused by distilled water washing.

CONCLUSIONS

1. The volume loading of the impregnated wood increased with increasing solution concentration. The volume loading of Chinese fir was higher than that of poplar when using the normal pressure and vacuum-pressure impregnation process, but lower when using the vacuum impregnation process.
2. Compared with air dried lumber and conventionally dried lumber, the volume loading of freeze dried lumber increased noticeably. The impact of the drying method was more notable on poplar than on Chinese fir.
3. The fixation effect of the B and P in poplar was lower by ultrasonic washing than that was by distilled water washing. The fixation effect was opposite in the Chinese fir.
4. Vacuum process was more suitable for the poplar (hardwood), and vacuum-pressure process was more suitable for the Chinese fir (soft wood). This results may provide the basis for the wood preservative technology.

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