EFFECTS OF ROSIN SIZING AGENT ON THE FIXATION OF BORON IN *STYRAX TONKINENSIS* WOOD

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SUMMARY

The aim of this study was to evaluate the effect of rosin sizing agent upon fixing boron in *Styrax tonkinensis* (Piere) wood treated with mixtures of 3% boric acid and 1% rosin sizing agent. After treatment, wood samples were also analyzed by scanning electron microscope observation and energy-dispersive X-ray spectroscopy (SEM-EDX). The results showed that all boron-rosin formulations impregnated *Styrax tonkinensis* wood evenly penetrated into the wood blocks. Boron-rosin treatment decreased by 16% the amount of boron leaching from treated wood samples compared with those from the samples treated with boric acid alone. The SEM-EDX analysis proved that the boron element was still in the cell lumens of boron-rosin treated wood blocks after leaching. Results indicated that rosin emulsion sizing agent can have an effect on the fixation of boron in wood. This signifies that using of rosin as fixing agents may contribute to lead to wood treated with boron based preservatives being more widely used.

Keywords: Boron, boron-rosin, leaching resistance, rosin.

I. INTRODUCTION

Boron compounds exhibit good biocidal activities when used in wood preservative formulations. Nevertheless, they have limited utility in outdoor applications due to their high solubility in water which cause leaching from impregnated wood (Yalinkilic, 2000). Therefore, several xation systems to limit or decrease boron leachability from treated wood have been developed. For example a combination of boron with: glycerol/glyoxal, vinyl monomers, silanes, alkydes, tall oil derivates, protein, water repellent compound, lique ed wood, and montan wax emulsions (Köse *et al.*, 2011; Obanda *et al.*, 2008; Lesar *et al.*, 2009, 2012; Sen *et al.*, 2009; Temiz *et al.*, 2008; Tomak *et al.*, 2011). However, due to the high costs or a two-step treatment, the above-mentioned approach could have not been deployed in practice.

Rosin is a product obtained from pines and some other plants. It is abundant, natural, and renewable. The major component of rosin is abietic acid, a partially unsaturated compound with three fused six-membered rings and one carboxyl group (Song, 2002). Therefore, it has a good hydrophobic property. Over the years, rosin was extensively applied in the paper industry as a sizing agent (Zhang, 2005). In our earlier investigations, the rosin sizing agent was used to impregnate poplar wood and the results showed that the rosin sizing agent can reduce the moisture absorption ability of poplar wood and contributes to improving wood decay resistance (Nguyen *et al.*, 2012; Li *et al.*, 2009, 2011). This paper presents results from a preliminary study to reduce the leachability of boron using a naturally dirived product - the rosin sizing agent to develop new formulations for wood preservation.

II. RESEARCH METHODOLOGY

2.1. Material preparations

Styrax tonkinensis (Piere) wood was selected according to the Chinese standard GB 1929 (2009) (same as ISO 3129). Wood specimens were cut from untreated *Styrax tonkinensis* sapwood into wood blocks with dimensions of 20 × 20 × 20 mm. Deficiency-free cubes were selected for the tests. The weight differences of the chosen blocks did not

exceed 0.5 g.

The anionic rosin emulsion sizing agent (R) was an industrial product and was supplied by Guangxi Wuzhou Arakawa Chemical Industries Co., Ltd. In this study, it was used to impregnate into wood at the concentration of 1%. And 3% Boric acid (H_3BO_3) was provided by Tianjin Kermel Chemical Reagent Co., Ltd., was used as a preservative salts. It was also combined with the rosin emulsion sizing agent to impregnate wood.

2.2. Treating wood blocks

Before treatment, all sapwood blocks were oven-dried at 103^{o}C overnight, weighed to the nearest 0.01 g and recorded as W_1. The blocks were then vacuum-treated with the treatment solution. The vacuum was applied for 30 min at 0.1 MPa before supplying the solution into the chamber. After the application another 30 min at 0.1 MPa vacuum diffusion period followed. Then, the blocks were kept in the treatment solution at ambient conditions until complete saturation. The blocks were then individually removed from the solution, wiped lightly to remove solution from the wood surface, and immediately weighed to the nearest 0.01 g to determine the mass after impregnation (W_2). The theory retention of each block was calculated using the following formula:

$$\text{Theory retention, kg/m}^3 = \frac{GC}{V} \times 10 \qquad (1)$$

Where $G = W_2 - W_1$ is the weight in grams of the treating solution absorbed by the block, C is the weight (g) of preservative in 100 grams of treating solution, and V is the volume of the block in cubic centimeters.

After calculating the retention, the treated samples were air-dried for 48 hours, and oven-dried at 103 °C overnight, and then weighed to determine the dry weights of the wood blocks after treatment. The difference between the dry weights before and after treatment is the actual retention of each block. And the percentage of actual retention to the theory retention was regarded as the treatability of each preservative formulation.

2.3. Leaching treated wood blocks

Leaching of boron was determined according to the standard of the American Wood Preservers' Association E11 (AWPA E11 2007). Twelve blocks per treatment were air-dried, then immersed in beakers of distilled water over which a vacuum was applied for 30 min. Then the vacuum was released and the wood blocks were immersed in the distilled water. After 6 h, 24 h, 48 h, and 48-h intervals the leaching water was removed and replaced with an equal amount of fresh distilled water. Leaching was carried out for a total of 14 days. All leachates were collected and kept for boron analysis.

2.4. Boron analysis

In order to measure the contents of boron leached from the treated wood blocks, the leachates were analyzed by using the azomethine-H method described by John *et al.* (1975) and following American Wood Preservers' Association standard method AWPA A2-07.

2.5. Microscopic observation

Small samples of dimensions 10 × 10 × 1 mm were cut from the untreated control and the treated wood blocks, and located 3 mm from each radial, tangential, and transverse surface of the wood block. Each sample was mounted on a metal stub with adhesive, and then they were placed under vacuum and were sputter-coated with a thin layer (approximately 20 nm thick) of gold. The samples were then observed with a scanning electron microscope (SEM, FEI Quanta 200, USA) at an accelerating voltage of 20 kV. Random observations were made on different structures to identify the existence of boron in the anatomical structure of the samples. The

element compositionwas determined by regional analysis using an energy dispersive X-ray spectrometer (EDX) combined with the SEM.

III. RESULTS AND DISCUSSION

3.1. Retention results

Retention levels of *Styrax tonkinensis* wood samples treated with boron-rosin solutions (as kilograms per cubic meter) and the actual percent retention of preservative formulations in wood blocks are recorded in Table 1. Total uptake of the treating solution in *Styrax tonkinensis* wood, including both rosin alone and in combination with boron, were relatively uniform. The actual retention of the rosin sizing agent alone or boron-rosin preservative was very close to theory retention. The actual percent retention of preservative solution containing rosin only or containing boric acid was 92.97% and 97.74%, respectively. However, when rosin sizing agent combined with boric acid to impregnate wood, the actual percent retention of presevative solution was 96.41%. Results indicate that the concentration of the solutions considered to impregnate *Styrax tonkinensis* wood using the impregnation method described did not influence the penetration of the preservative complexes into the wood blocks. Which could be proved by SEM analysis.

Table 1. Retention levels and treatability of wood samples treated with boron-rosin solutions

Abbreviation	Concentrations	Theory Retention (kg/m^3)	Actual Retention (kg/m^3)	Treatability[a] (%)
1	1% R + 3% H_3BO_3	26.15 (1.07)[b]	25.20 (2.77)	96.41 (10.31)
2	3% H_3BO_3	17.12 (0.97)	16.74 (1.66)	97.74 (7.71)
3	1% R	6.47 (0.47)	6.01 (0.68)	92.97 (9.59)

Note: [a]Treatability refers to the percentage of actual retention to the theory retention.
[b] All results are means of 24 samples. Standard deviations are in brackets.

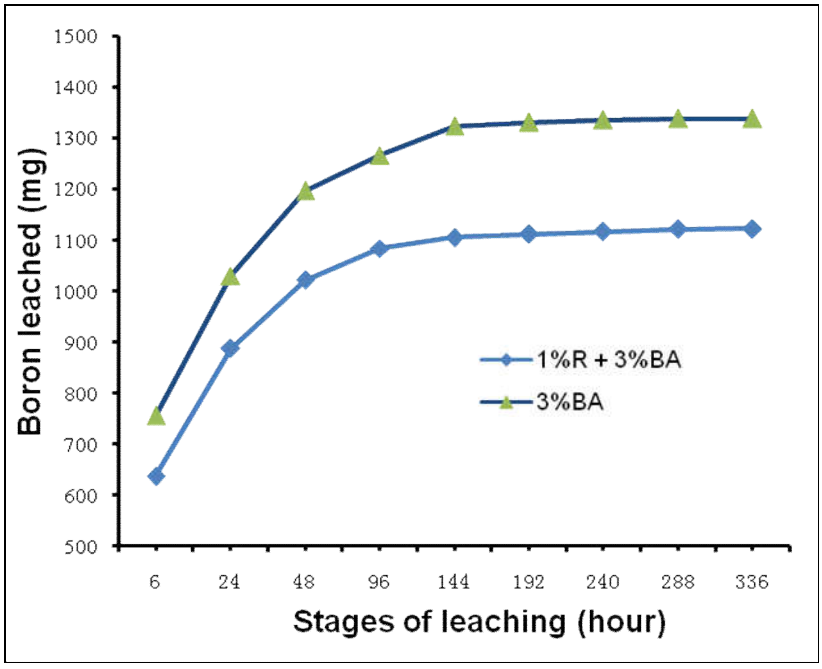

Figure 1. Boron released from the treated wood samples at different time intervals (BA: boric acid (H_3BO_3), R: rosin sizing agent)

3.2. Boron leaching

The amount of boron ions released from the wood samples treated with boric acid solution alone or in combination with rosin at different time intervals are presented in Figure 1. The results show that a large amount of boron ions was leached out from the wood samples treated with boric acid alone. After 14 days of leaching, 1338 mg of boron was leached out from the samples. However, after 1% rosin sizing agent was added, the observed leaching of the boron was 1122 mg, in comparison to the treated samples with boric acid alone, the extent of boron leaching reduced was 16%. These results suggest that the rosin can contribute to improving boron fixation in wood. This was probably due to the hydrophobic property of rosin. After having penetrated into the wood blocks, the rosin molecules present in the cell lumen and forming an adhesive lm that covers the boron crystals (Nguyen *et al.*, 2013). During the leaching process, the rosin acted as a barrier that slowed down boron release from deep inside of the samples, which resulted in the reduction of the boron ion diffusing from wood during the leaching process.

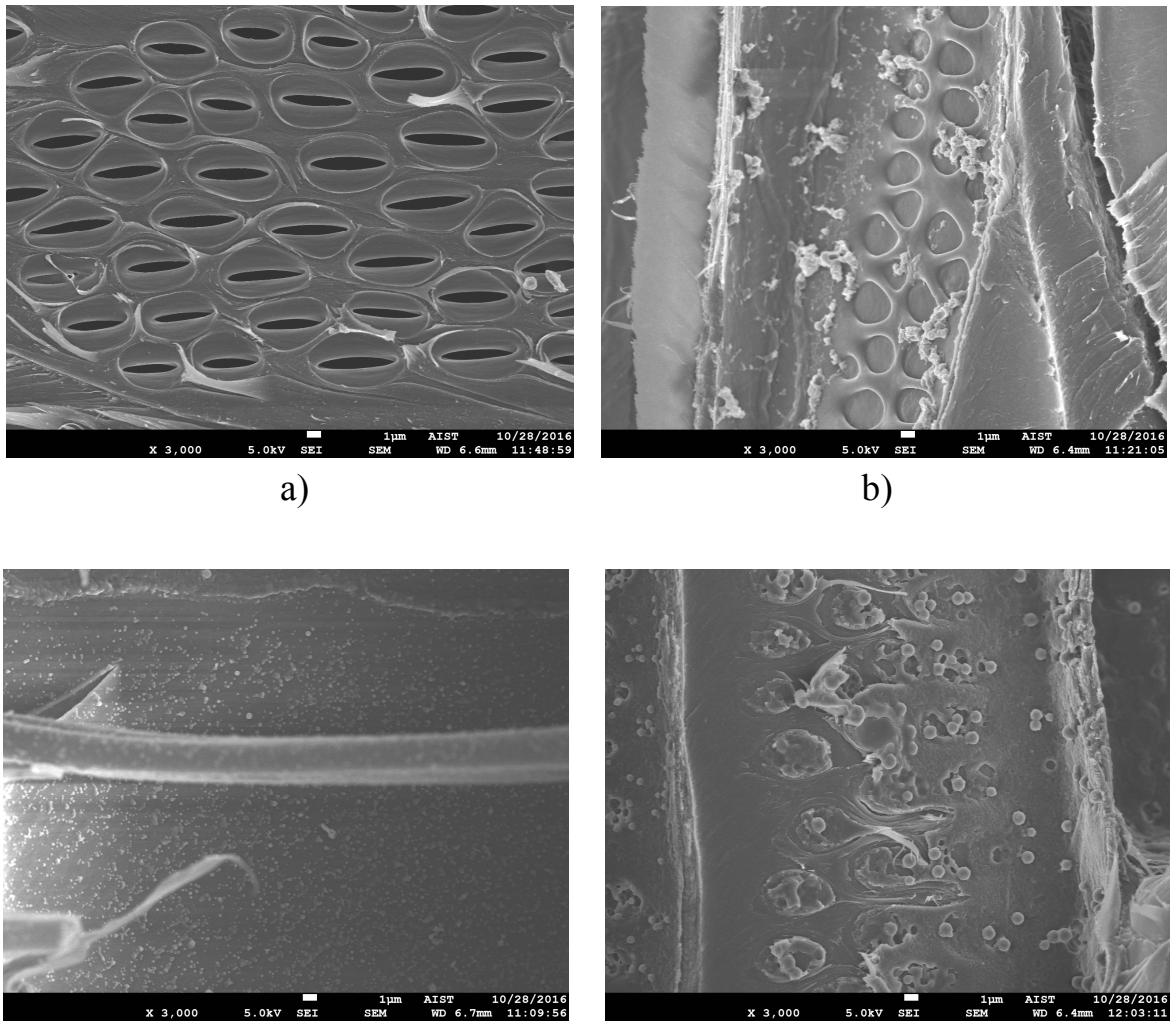

Figure 2. SEM images of tangential section of control wood block (a) and boric acid alone (b), rosin alone (c) and boron-rosin treated wood samples (d)

3.3. Microscopic observation

Figure 2 shows the SEM images of the wood sample before and after treatment. untreated control and wood samples treated with boron-rosin solutions. It can be clearly seen that surface of wood cell wall of the control sample was extremely smooth and no preservative complexes was detected in any part of the untreaed control wood blocks (Fig. 2a). When the wood blocks treated with only boric acid were observed, various crystal particles were found in the cell lumens (Fig. 2b). The spot analysis using SEM-EDX proved that these particles contained B (Fig. 3ab). When the wood blocks treated with rosin alone, various spherical agglomerates were easily detected in the cell lumen (Fig. 2c). However, unlike the crystals in Figure 2b or spherical agglomerates in Figure 2c, various spherical agglomerates were easily detected in the cell lumen of the wood blocks treated with boron-rosin formulation, these agglomerates were tightly adhered to the wood cell wall (Fig. 2d). The spectrum obtained from the spot analysis confirmed that these agglomerates contained the element B and they had a lower B content in comparison to that observed in the crystal particles (Fig. 3cd). This signifies easily penetrated into the wood blocks.

Figure 4 shows SEM images corresponding spectrum of tangential sections of treated wood blocks after leaching. For wood blocks treated with boric acid alone, after leaching no crystal particles was detected by SEM observation (Fig. 4a). This revealed that after leaching, boric acid seemed to be completely leached out from treated wood. However, when the leached wood blocks treated with boron-rosin were observed, the spherical agglomerates were still detected in the cell lumens (Fig. 4b). In addition, the spot analysis using SEM-EDX proved that these agglomerates contained the element B (Fig. 4cd). This signi es that the rosin formed an adhesive lm to cover the boron crystals and the resulting boron was xed into the wood blocks.

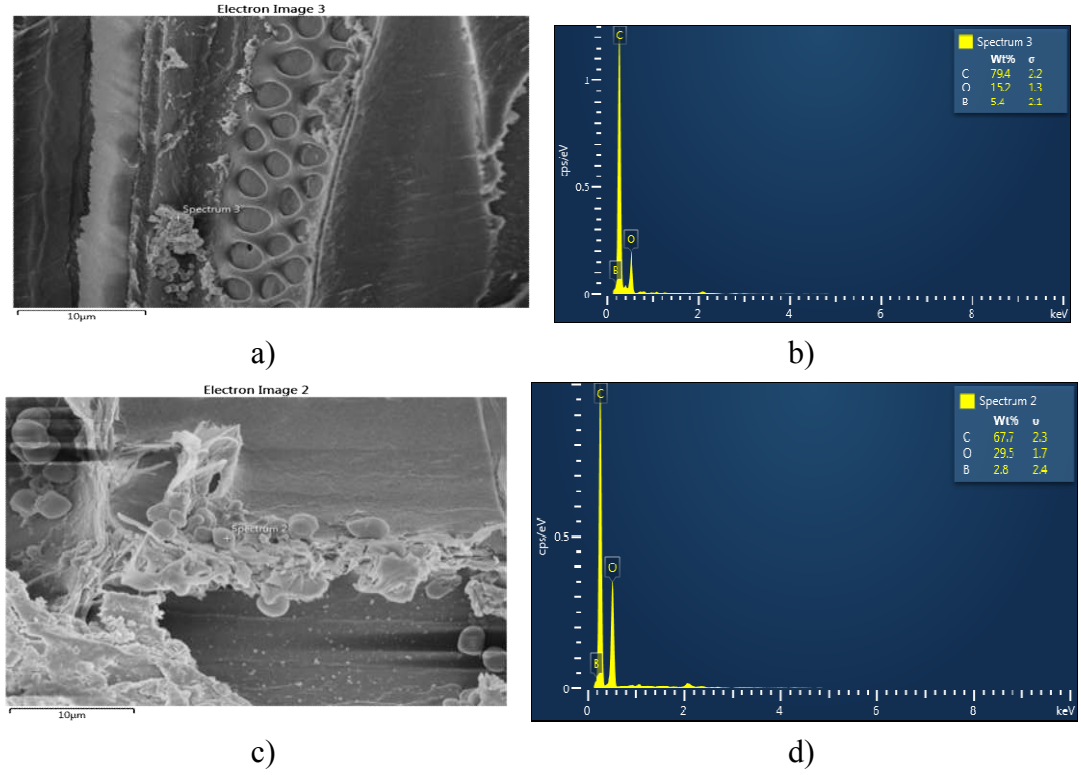

Figure 3. SEM images (left) and corresponding spectrum (right) of tangential section of unleached wood blocks treated with boric acid alone (a,b) and boron-rosin solution (c,d)

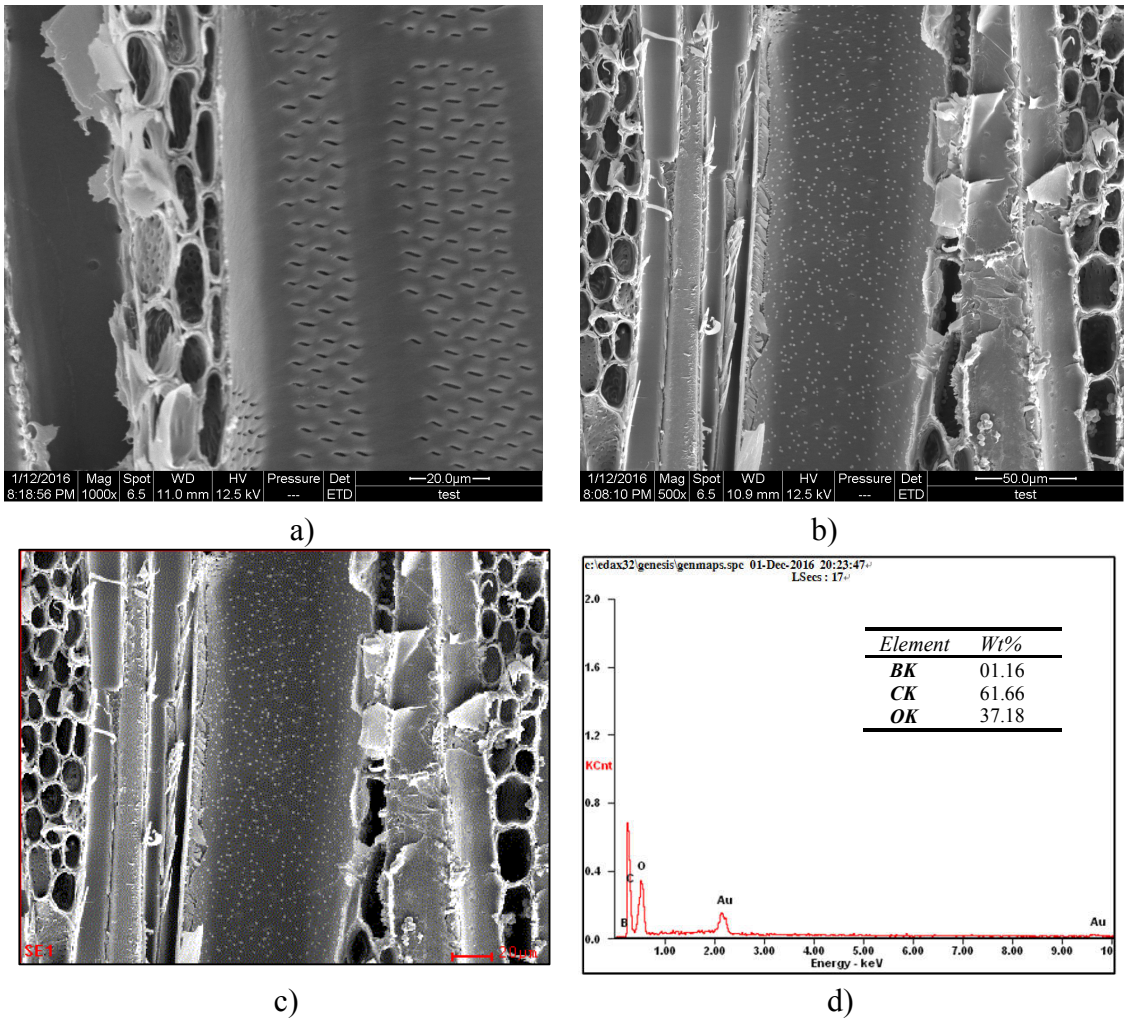

Figure 4. SEM images and corresponding spectrum of tangential section of leached wood blocks treated with boron alone (a) and boron-rosin solution (b, c, d).

IV. CONCLUSIONS

This study evaluated the effect of rosin sizing agent on the fixation of boron in *styrax tonkinensis* wood. The results showed that using rosin alone or in combination with boric acid solution to impregnated *Styrax tonkinensis* wood by the impregnation method described did not influence the penetration of the preservative complexes into the wood blocks. The rosin sizing agent had have a certain effect on the fixation of boron in wood. The amount of boron ions released from the samples treated with the boron-rosin solution reduced by 16% compared with those from the samples treated with boric acid alone. The SEM-EDX analysis of the wood blocks treated with boron-rosin formulation confirmed that the preservative complexes containing B still existed in the cell lumens of wood, even after leaching. The use of rosin as fixing agents may contribute to lead to wood treated with boron based preservatives being more widely used.

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ẢNH HƯỞNG CỦA KEO NHỰA THÔNG ĐẾN KHẢ NĂNG CỐ ĐỊNH BORON TRONG GỖ BỒ ĐỀ

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TÓM TẮT

Mục đích của nghiên cứu này là đánh giá ảnh hưởng của keo nhựa thông đến khả năng rửa trôi của boron từ gỗ Bồ đề được xử lý bởi hỗn hợp của 3% axit boric và 1% keo nhựa thông. Các mẫu gỗ sau khi xử lý được quan sát và phân tích bằng một phổ kế tán sắc năng lượng tia X kết hợp với kính hiển vi điện tử (SEM-EDX). Kết quả cho thấy rằng tất cả các công thức boron - nhựa thông được ngâm tẩm vào gỗ Bồ đề đều thẩm thấu tốt vào các mẫu gỗ thí nghiệm. Gỗ được xử lý bởi công thức kết hợp boron-nhựa thông đã giảm 16% lượng boron bị rửa trôi so với khi chỉ sử dụng axit boric để xử lý. Kết quả phân tích SEM-EDX cũng đã chứng minh nguyên tố B vẫn tồn tại trong khoang tế bào của gỗ được xử lý bởi boron-nhựa thông sau khi rửa trôi. Kết quả đã cho thấy rằng dung dịch keo nhựa thông có một ảnh hưởng nhất định đến khả năng cố định boron trong gỗ. Điều này gợi ý rằng sử dụng nhựa thông để làm chất cố định có thể góp phần nâng cao khả năng sử dụng của gỗ được xử lý bởi các hợp chất chứa boron.

Từ khóa*:* Boron, boron-nhựa thông, kháng rửa trôi, nhựa thông.

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