EFFECTS OF ROSIN SIZING AGENT ON THE DIMENSIONAL STABILITY OF *Styrax tonkinensis* WOOD

Nguyen Thi Thanh Hien[1], Tran Van Chu[2]
[1,2] *Vietnam National University of Forestry*

SUMMARY
Wood protection efficacy of boron compounds against biological agents, flame retardancy, and suitability to the environment is well known. Nevertheless, they have limited utility in outdoor applications due to their high solubility in water which cause leaching from impregnated wood. Rosin is a product obtained from pines and some other plants. It is abundant, natural, and renewable. Over the years, rosin has been widely used in the paper industry as a sizing agent. Moreover, rosin sizing agent was also demonstrated to have a certain effect on the fixation of boron in wood. Therefore, the aim of this study was to evaluate the effect of rosin upon dimentional stability of styrax wood treated with mixtures of 3% boric acid and 1.0%, 2.0%, or 4.0% rosin sizing agent. The results indicated that all rosin-boron treatments decreased the moisture absorption, water absorption and swelling properties of wood, whilst increasing water repellent efficiency and anti-swelling efficiency to approximately 30% after 30-day immersion in water. This result showed that the use of rosin alone or combination with boron to impregnate styrax wood could reduce swelling of wood due to water/moisture absorption during use and contribute to increased dimensional stability of wood.
Keywords: Dimensional stability, rosin-boron, rosin sizing agent, styrax, water repellent.

1. 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 fixation 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, liquefied wood, and montan wax emulsions (Obanda *et al.*, 2008; Temiz *et al.*, 2008; Lesar *et al.*, 2009; Sen *et al.*, 2009; Köse *et al.*, 2011; Tomak *et al.*, 2011; Lesar *et al.*, 2012). However, due to the high costs or a two-step treatment required, the above-mentioned approach could have not been deployed in practice.

Rosin is a product obtained from pines and some other plants, mostly conifers. It is abundant, natural, and renewable. One of the major components of rosin is abietic acid, a partially unsaturated compound with three fused six-membered rings and one carboxyl group, giving it good hydrophobic properties. Over the years, rosin has been the most widely used in the paper industry as a sizing agent (Yao and Zheng, 2000). The new approach and reaction mechanisms between carboxylic acid groups of resin acids of rosin and copper have been investigated by Pizzi (1993a), and wood blocks treated with solutions of rosin-copper soap using benzene or ethanol as solvents have shown to be effective against both fungal and termite in field tests (Pizzi, 1993b). In another report, Roussel used non-solvent rosin-copper formulations to impregnate wood (Roussel *et al.*, 2000) and treated wood blocks have shown good performance when leached, but a double impregnation system was required. In addition, our earlier investigation showed that rosin sizing agent had a certain effect on fixation of copper in wood, after being treated with the mixture of rosin sizing agent and $CuSO_4$, wood blocks still had great decay resistance, even after leaching (Nguyen *et al.*, 2012; 2013). Recently, rosin sizing agent was also demonstrated to have a certain effect on the fixation of boron in wood (Nguyen and Li, 2017). Therefore, the aim of this research work was to evaluate the effects of rosin sizing agent on the dimension stablity of styrax wood through some characteristics, such as moisture absorption and water absorption and swelling of wood after treated with the mixture of rosin sizing agent and boric acid. This is primary criteria for the selection and designing of wood for different applications.

2. RESEARCH METHODOLOGY

2.1. Preparation of test specimens and treating solutions

Styrax wood (*Styrax tonkinensis* Piere) was selected according to ISO 3129. Wood samples were prepared from untreated styrax sapwood. The specimen dimension were 20 × 20 × 20 mm (longitudinal, tangential, and radial, respectively). Defect-free specimens were selected for the tests. Samples were divided into eight groups: one untreated group served as a control, and the other seven groups were treated with acid boric and rosin sizing agent, separately or in combination.

The anionic rosin emulsion sizing agent was an industrial product and was supplied by Guangxi Wuzhou Arakawa Chemical Industries Co., Ltd. In this study, rosin was used at three concentration levels (1.0, 2.0, and 4.0%). Boric Acid (H_3BO_3) was used as a preservation to protect wood at only one concentration of 3%. The other chemical reagents used in this work were provided by Tianjin Kermel Chemical Reagent Co., Ltd and were all pure grade reagents.

2.2. Impregnation procedures

Wood samples were oven dried at 103°C for 24 hours before being weighed. After drying, the samples were treated using a full-cell pressure process at 0.7 MPa pressure for 2 hours. Following this, the samples remained in the solutions for 60 minutes at atmospheric pressure. The wood samples were then removed from the treatment solution, wiped lightly to remove the rest of the solution from the wood surface, and weighed (nearest 0.01 g) to determine gross retentions for each treating solution.

All treated samples were subsequently stored at ambient laboratory temperature to air drying for 4 weeks prior to testing.

2.3. Microscopic observation

After treatment, small samples (10 × 10 × 1 mm) were cut from the untreated control and treated wood blocks using a razor blade. The samples were mounted on a metal stub with adhesive, and then placed under vacuum and sputter-coated with a thin layer (approximately 20 nm thick) of gold. The samples were then observed with a scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM, FEI Quanta 200; USA) at an accelerating voltage of 20 kV.

2.4. Measurement of moisture absorption

The treated samples (20 × 20 × 20 mm) were oven-dried at 103±2°C for 24 h and weighed to determine the oven-dry weight. After drying, the wood samples were placed in a temperature and humidity-controlled chamber at 20°C and 65% RH for approximately 4 weeks. After stabilization, each sample was weighed using a digital balance. The equilibrium moisture content (EMC in %) was calculated using the following equation:

$$\text{EMC (\%)} = [(G - G_o)/G_o] \times 100 \quad (1)$$

where G was the equilibrium weight of sample after moisture absorption (g), G_o was oven-dry weight of wood sample (g).

2.5. Measurement of water absorption and dimensional stability

Oven-dry wood samples (20 × 20 × 20 mm) were placed into a 1000 mL beaker filled with distilled water. The samples were placed separately and horizontally in the beakers with stainless steel mesh over the specimens. The specimens were removed from the beaker after 6h, 1 day, 2 days, 4 days, 8 days, 12 days and 20 days, and thereafter at 10-day intervals and excess water was removed by dabbing with a tissue. The samples were weighed and again placed in the beaker and the water replaced. The test was continued for a total of 30 days. The radial, tangential, and volumetric swelling at both the water swollen and oven-dried states were measured using a digital micrometer (±0.01 mm). The swelling difference between treated and control samples was used to calculated the anti-swelling efficiency (ASE) according to the following formula:

$$\text{ASE (\%)} = \frac{S_u - S}{S_u} \times 100 \quad (2)$$

where S_u was volumetric swelling of untreated wood (%) and S was that of treated wood (%).

$$S (\%) = [(V_w - V_d)/V_d] \times 100 \quad (3)$$

where V_w was volume of the wood sample after saturation with water (mm^3) and V_d was the volume of initial dry wood sample (mm^3).

The swelling coefficient in the radial and tangential direction was also calculated as,

$$S_\alpha (\%) = [(\alpha_w - \alpha_d)/\alpha_d] \times 100 \quad (4)$$

where α_d was the single direction dimensional (radial or tangential) of the initial dry sample (mm) and α_w was the single direction dimension after saturation with water (mm).

Water absorption (WA) was calculated according to the following formula:

$$WA (\%) = [(W_2-W_1)/W_1] \times 100 \quad (5)$$

where W_2 was the wet weight of the sample after wetting with water (g) and W_1 was the initial dry weight of the sample (g).

Water repellency efficiency (WRE) was calculated according to the following formula:

$$WRE (\%) = [(W_{ac} - W_{at})/W_{ac}] \times 100 \quad (6)$$

where W_{at} was the water absorption rate of treated wood samples (%), and W_{ac} was the water absorption rate of untreated control (%).

2.6. Statistical Analysis

In order to determine the effects of wood preservatives on dimensional stability of wood, one-way ANOVA tests were conducted and homogeneous groups were determined by using SPSS 20.0 statistical software package.

3. RESULTS AND DISCUSSION

3.1. Moisture absorption

The resultant equilibrium moisture content (EMC) of wood samples impregnated with boric acid and rosin sizing agent, separately or in combination are provided in figure 1. In comparison to untreated samples, all treatments affected EMC of wood. EMC value of untreated samples averaged 10.37%, while EMC's of samples treated with 1%, 2%, or 4% rosin were 9.72%, 9.59%, and 9.66%, respectively. Samples impregnated with 3%H_3BO_3 plus 1%, 2%, or 4% rosin had EMC values of 10.30%, 10.29% and 10.02%, respectively, suggesting that EMC decreased with increasing rosin concentration. This was probably due to the hydrophobic property of rosin. Increased rosin concentration leads to increased uptake as well as the filling of the lumen with rosin, which increasing water repellency, thus reducing the moisture absorbing capacity of the wood sample (Eberhardt *et al.*, 1994; Mansouri *et al.*, 2011). However, one-way ANOVA revealed that this difference was not significant (Table 1). Moisture absorption in samples treated with rosin alone or in combination with boron decreased significantly. The results also suggested that addition of rosin can contribute to increased dimensional stability of wood.

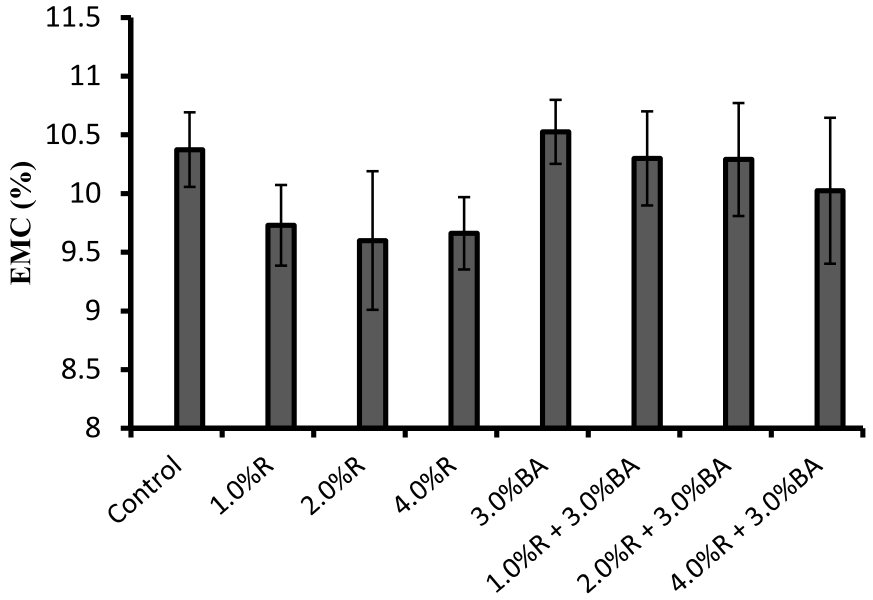


Figure 1. EMC (%) of untreated controls and samples treated with rosin sizing agent (R) alone or in combination with boric acid (BA)

Table 1. Equilibrium moisture content (EMC), water absorption (WA) and water repellent efficiency (WRE) of styrax wood treated with rosin alone and in combination with boron

Treatments	Retention (Kg/m^3)	EMC (%)	WA (%)	WRE (%)
1.0%R	5.77 (0.43)	9.72 (0.34)^{ab}	118.03 (7.31)^{a}	29.06
2.0%R	9.85 (0.53)	9.59 (0.59)^{a}	121.18 (8.27)^{a}	27.16
4.0%R	22.19 (1.70)	9.66 (0.31)^{ab}	159.61 (7.51)^{bc}	4.07
3.0%BA	12.72 (1.59)	10.53 (0.27)^{d}	165.11(10.23)^{bc}	0.76
1.0%R + 3.0%BA	22.27 (1.39)	10.30 (0.40)^{cd}	157.07 (9.38)^{b}	5.59
2.0%R + 3.0%BA	27.41 (1.06)	10.29 (0.48)^{cd}	156.89 (10.78)^{b}	5.70
4.0%R + 3.0%BA	37.96 (3.50)	10.02 (0.62)^{bc}	161.50 (7.77)^{bc}	2.93
Control	-	10.37 (0.32)^{cd}	166.37 (7.83)^{c}	-

Note: Standard deviations are in brackets; BA: Boric acid and R: rosin sizing agent; Means within a column followed by the same letter are not significantly different at 5% level of significance using the one-way ANOVA test.

3.2. Water absorption and water repellent efficiency

Relative water absorption (WA) levels of wood samples treated with boric acid and rosin sizing agent, separately or in combination measured at different time intervals are presented in figure 2. Water uptake for both control and treated samples increased rapidly from the start of soaking to approximately 8 soaking days, after which the rate of increase decreased significantly. These results may be due to WA into available empty pores in wood at the beginning of soaking and the reduction of those wood spaces over time. However, the increased rate of water uptake for treated wood was much lower than that for controls, throughout the soaking time. After 30 days immersion in water, total water absorption level of untreated control samples was 166.37% and boric acid only treated samples was 165.11% (Table 1). However, rosin application reduced the WA level of treated wood, particularly in samples treated with rosin sizing agent solutions had WA level in the range of 118.03% to 159.61%. This improvement could be attributed to the hydrophobic property of rosin and the formation of rosin deposits in the cell lumen, which created a physical and mechanical barrier that hindered water movement (Nguyen *et al.*, 2012; Nguyen and Li, 2017). Furthermore, micrographs SEM of the treated Styrax wood (Figure 3) clearly showed that the rosin and rosin-boron compound filled the vessels as well as lumens, and other void spaces in the wood structure. This reduced penetration of water into the wood blocks.

Water repellent efficiency (WRE) values of the treated samples after 30 days of water immersion are shown in table 1. Samples with lower water uptakes produced higher WRE. Samples treated with rosin alone or in combination with boron had reduced the WA and improved WRE. When the concentration of rosin increase from 1.0 to 4.0% in the impregnation solution, the WRE values decreased from 29.06 to 4.06%. This was probably due to using pressure method to impregnate wood samples. The increase of rosin concentration leads to increase in uptake, and also leads to an increased amount of rosin in the outer part of the wood sample due to increasing filtration effect. After impregnation, the outer part of the wood sample is cleaned carefully, and therefore a relatively larger amount of rosin is removed from the wood surface at higher concentrations of rosin, which might be partially responsible for decreasing the WRE values. The analysis of variance (ANOVA) revealed that there was a significant difference in WA values and the water repellent efficiency (WRE) between untreated control and samples treated with rosin or rosin-boron formulations. However, there were no significant differences in WA values between samples treated with 1% rosin and 2% rosin nor significant differences between samples treated with boric acid alone and samples treated with rosin-boron formulations (Table 1).

This result revealed that using rosin sizing agent to treat syrax wood could improved water repellent of wood and the highest increment of WRE was observed in samples treated with 1% rosin sizing agent.

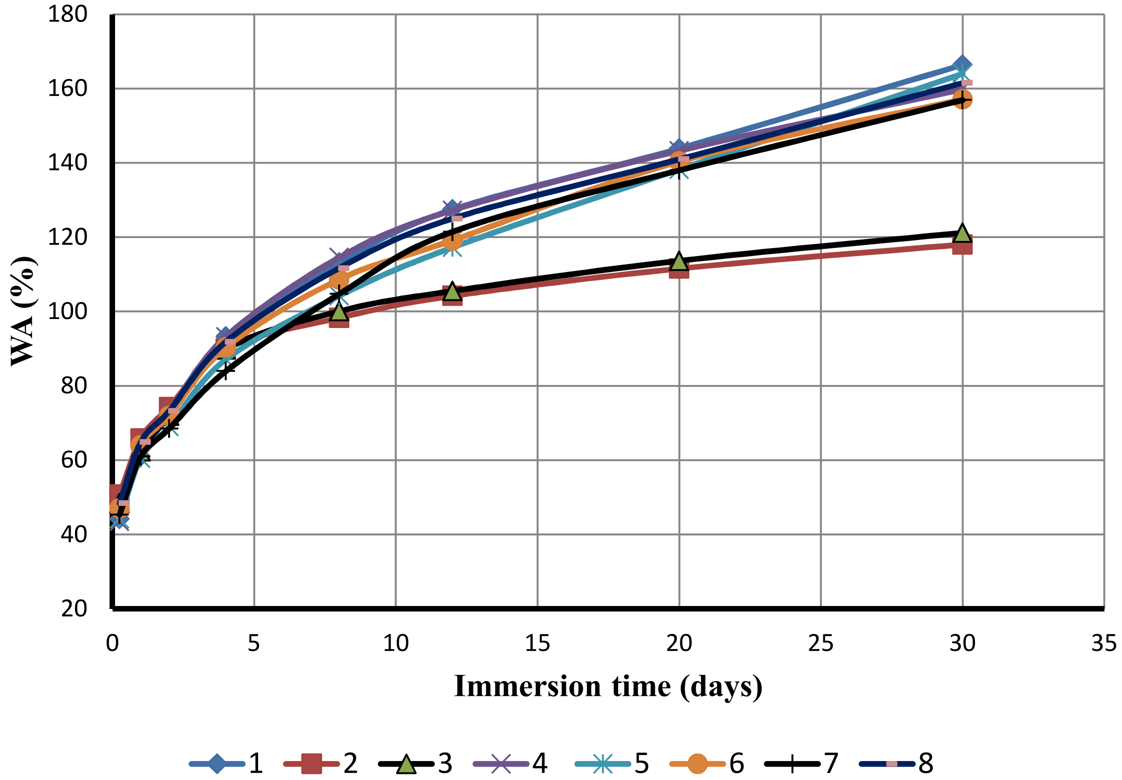


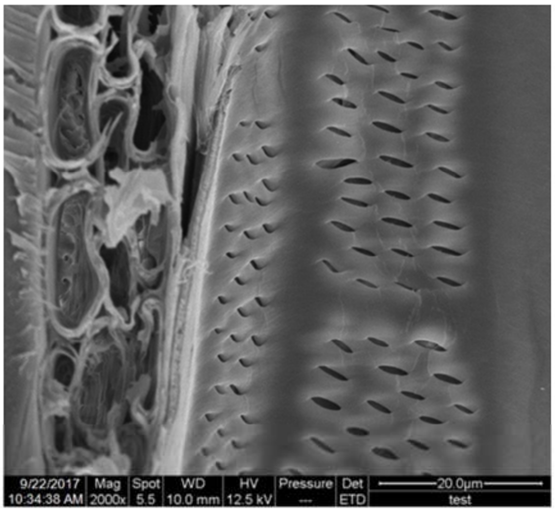
Figure 2. Changes in water absorption of untreated controls and samples treated with rosin alone or in combination with boron during water immersion (%)

(1: Control; 2: 1% R; 3: 2% R; 4: 4% R; 5: 1% R + 3% BA; 6: 2% R + 3% BA; 7: 4% R + 3% BA; 8: 3% BA)

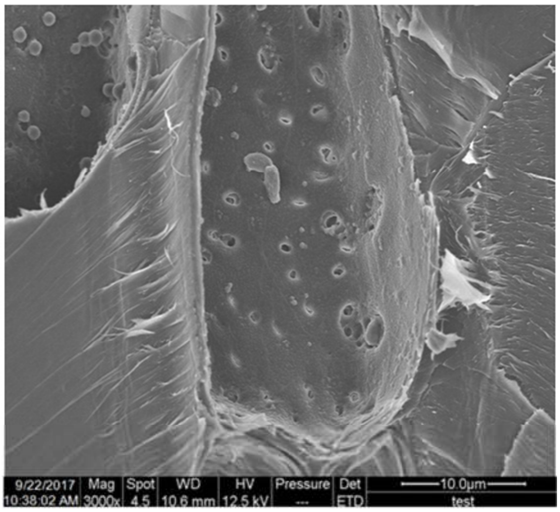
3.3. Swelling properties and anti-swelling efficiency (ASE)

The results of swelling (S) in the radial, tangential directions, and volumetric of the untreated control and treated styrax wood samples after a 30 day water immersion are presented in figure 4. Untreated samples exhibited higher swelling coefficient values compared to the treated wood samples. Average swelling in the radial, tangential, and volumetric for the controls were 3.7%, 7.5%, and 11.8%, respectively and for samples treated with boric acid alone were 3.55%, 6.73% and 10.53%. However, the samples treated with rosin sizing agent alone or in combination with boron had the swelling in the radial range from 3.03% to 3.37%; from 5.41% to 6.38% in the tangential and from 7.92% to 9.81% in the volumetric. Overall, all treatments apply rosin sizing agents in this study improved the swelling coefficient of wood and the concentration of rosin sizing agent increase from 1.0 to 4.0%, the swelling coefficient values slightly increased. However, the analysis of variance (Table 2) revealed that there were signification differences for swelling in the tangential and volumeric between untreated control and the rosin alone or rosin-boron treated samples. But the rosin sizing agent concentrations used in this study had no significant impact on swelling of wood and there was no significant differences for swelling in the radial between untreated control and treated samples.

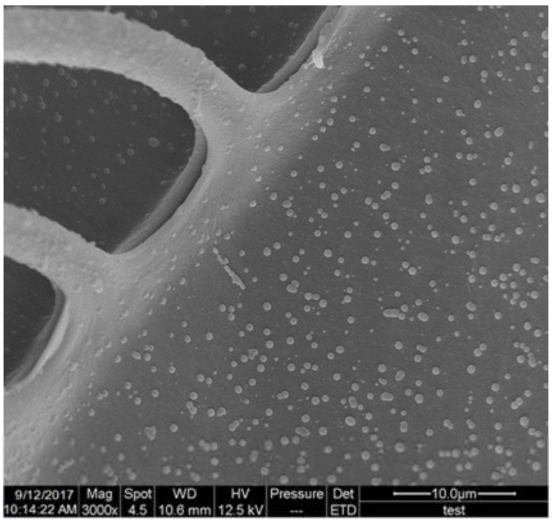
The anti-swelling efficiency (ASE) values based on average values of swelling coefficients are also summarized in table 2. All samples treated with rosin sizing agent alone or in combination with boric acid expressed significant improvement in ASE compared to untreated samples. This may reflect the fact that rosin has good hydrophobic properties and after penetrated into the wood samples, the rosin molecules formed spherical agglomerates in the cell lumen (Figure 3) that blocks water molecule movement inside the wood cell wall. This result showed that wood samples treated with rosin alone or rosin-boron compounds could reduce swelling of wood due to water/moisture absorption during use and contribute to increased dimensional stability of wood.



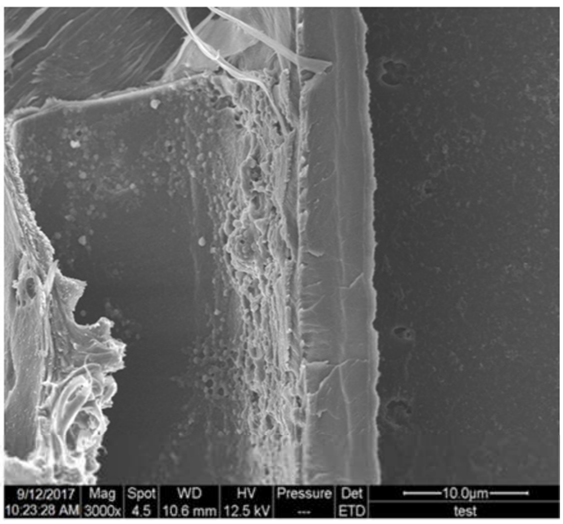
a)



b)



c)



d)

Figure 3. SEM images of tangential section of styrax samples treated with rosin alone and in combination with boron
(a - Control; b - 3% BA; c - 1% Rosin; d - 1% Rosin + 3% BA)

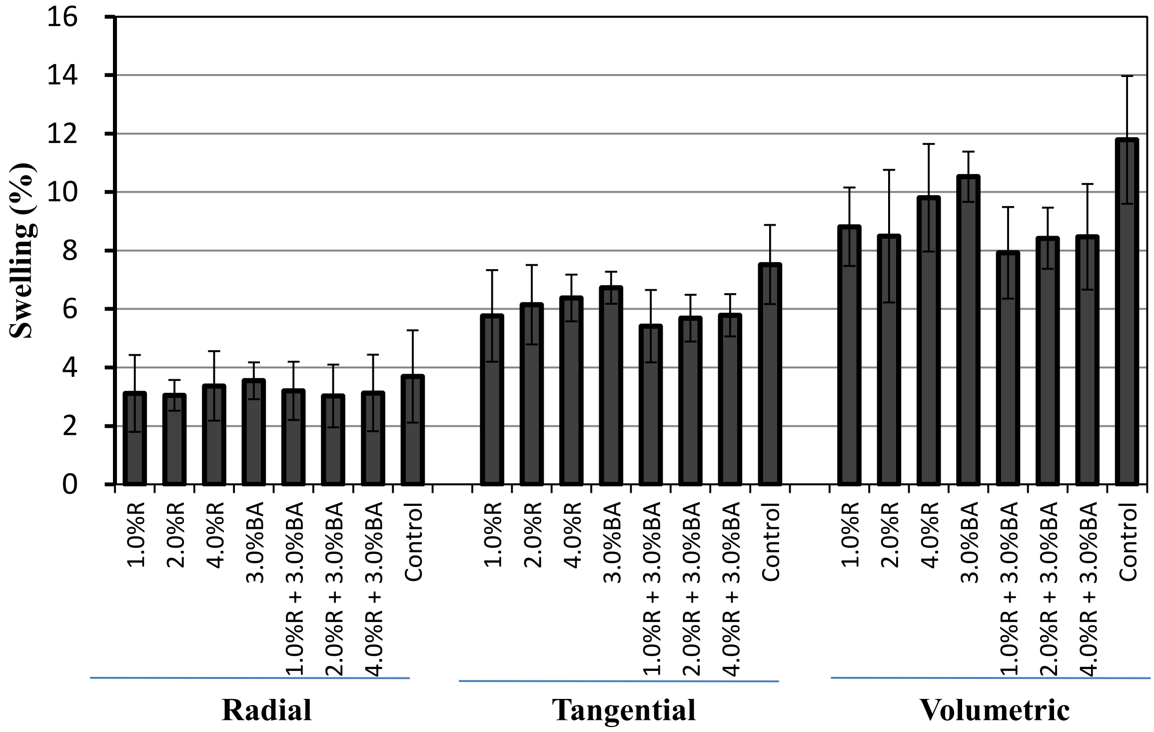


Figure 4. Swelling (%) of untreated controls and samples treated with rosin alone or in combination with boron after saturation with water (BA: Boric acid and R: rosin sizing agent)

Table 2. Effects of concentrations of rosin sizing agent on the dimensional stability of styrax wood after saturation with water

Treatments	Swelling (%)			ASE (%)		
	Radial	Tangential	Volumetric	Radial	Tangential	Volumetric
1.0%R	3.12^{a}	5.77^{a}	8.81^{ab}	15.68	23.29	25.24
2.0%R	3.05^{a}	6.15^{a}	8.49^{ab}	17.43	18.24	27.94
4.0%R	3.37^{a}	6.38^{a}	9.81^{bc}	8.90	15.13	16.78
3.0%BA	3.55^{a}	6.73^{bc}	10.53^{cd}	4.03	10.53	10.69
1.0%R + 3.0%BA	3.20^{a}	5.41^{a}	7.92^{a}	13.31	28.01	32.80
2.0%R + 3.0%BA	3.03^{a}	5.69^{ab}	8.42^{ab}	18.10	24.33	28.57
4.0%R + 3.0%BA	3.13^{a}	5.78^{ab}	8.47^{ab}	15.37	23.07	28.12
Control	3.70^{a}	7.52^{c}	11.79^{d}	-	-	-

Note: Means within a column followed by the same letter are not significantly different at 5% level of significance using the one-way ANOVA test.

4. CONCLUSIONS

This study evaluated effect of rosin on the moisture absorption, water absorption and dimension stability of styrax wood treated with rosin sizing agent alone or in combination with boric acid.

All samples impregnated with rosin sizing agents or rosin-boron formulations obviously decreased moisture absorption, water absorption as well as swelling of wood, whilst increased the WRE and ASE of wood to approximately 30% after 30-day immersion in water. The highest increment of WRE and ASE was obtained in samples treated with 1% rosin sizing agent. However, the concentration of rosin sizing agent used in this study did not significant affect moisture absorption and swelling of wood.

The use of rosin-boron formulatons to impregnate styrax wood could increase fixation of boron in wood, while could also improving dimensional stability of wood.

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ẢNH HƯỞNG CỦA KEO NHỰA THÔNG ĐẾN ĐỘ ỔN ĐỊNH KÍCH THƯỚC CỦA GỖ BỒ ĐỀ

Nguyễn Thị Thanh Hiền[1], Trần Văn Chứ[2]

[1,2]Trường Đại học Lâm nghiệp

TÓM TẮT

Hiệu quả bảo quản của các hợp chất chứa boron chống lại các sinh vật hại lâm sản, chống cháy và an toàn với môi trường đã được biết đến từ lâu. Tuy nhiên, nó lại bị hạn chế sử dụng ở ngoài trời do nó dễ bị hòa tan bởi nước, làm cho nó dễ bị rửa trôi. Nhựa thông là một sản phẩm đạt được từ các loại gỗ thông và một số loại gỗ khác. Nó rất phong phú, có nguồn gốc từ thiên nhiên và có thể tái sinh được. Nhiều năm qua, nhựa thông đã được sử dụng rộng rãi trong ngành công nghệ giấy làm tác nhân gia keo. Ngoài ra, keo nhựa thông cũng đã được chứng minh là có hiệu quả nhất định trong việc cố định boron ở trong gỗ. Vì vậy, mục đích của nghiên cứu này đánh giá ảnh hưởng của nhựa thông đến độ ổn định kích thước của gỗ bồ đề được xử lý bởi hỗn hợp của 3% axit boric và 1%, 2%, 4% keo nhựa thông. Kết quả cho thấy rằng, tất cả các xử lý bởi hỗn hợp nhựa thông-boron đều làm giảm khả năng hút nước, hút ẩm và khả năng dãn nở của gỗ, đồng thời làm tăng hiệu quả chống thấm nước và chống trương nở của gỗ lên khoảng 30% sau 30 ngày ngâm trong nước. Kết quả này đã cho thấy, sử dụng keo nhựa thông đơn lẻ hoặc kết hợp với boron để ngâm tẩm cho gỗ Bồ đề đã có thể làm giảm sự dãn nở của gỗ do hút ẩm và hút nước trong quá trình sử dụng, đồng thời góp phần làm tăng khả năng ổn định kích thước của gỗ.

Từ khóa: Bồ đề, keo nhựa thông, khả năng chống thấm nước, nhựa thông-boron, ổn định kích thước.

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