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ARTICLE

Evaluation of Weathering Performance of Rosin-Copper Based Treated Wood

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ABSTRACT

This study aimed to evaluate the effect of natural weathering on some surface characteristics and mechanical properties of Styrax wood treated with mixtures of 1.0%, 2.0%, or 4.0% rosin sizing agent and 3% copper sulfate. Wood samples after treatment were exposed to outdoor conditions for one year and changes in color, glossiness, weight loss, compression strength parallel to grain (CSPG), modulus of rupture (MOR), and modulus of elasticity (MOE) were investigated after 6 and 12-month of natural weathering. The results showed that rosin-copper treatment could improve color stability and gloss of samples after weathering. Mass losses of all rosin-copper treated samples after 12 months of exposure were negligible compared with the untreated control samples. In addition, rosin-copper treatment enhanced the CSPG compared to untreated controls, but slightly decreased the MOR and MOE of Styrax wood before weathering. Natural weathering factors induced a reduction for all strength properties, however, the decrease rate for strength properties of rosin-copper treated samples was negligible compared with the untreated control samples after 12-month natural weathering exposure. The FTIR and SEM-EDX confirmed that the use of the rosin-copper formulations to impregnate wood could decrease the hazard of the copper preservative leaching into the environment, while also enhancing more resistance against weathering factors and other biotic factors.

KEYWORDS

Rosin-copper; weathering; color stability; CSPG; MOR; MOE

1 Introduction

When wood is used outdoors, a variety of ambient factors degrade the main wood constituents such as fungi, insects, dimensional instability, and weathering. The term wood weathering describes a combination of UV degradation, temperature, humidity, and atmospheric pollutants (e.g., acid rain, nitrogen oxides, ozone, and sulfur dioxide) [1]. The ultraviolet (UV) component of sunlight and fluctuations in humidity are the main agents for wood weathering [2]. The effect of wood weathering is represented by initial wood surface color changes followed by cracking, roughening, loss of gloss, and are also accompanied by the alteration of physical, mechanical, chemical properties of wood [1,3].

Wood can be protected against weathering and attack by organisms as well as other wood-damaging agents applying preservatives and modification of wood. For example, treatment with copper compounds to enhance the durability of wood has been investigated from the early nineteenth century and is still in use today [4]. Some waterborne preservatives such as chromate copper arsenic (CCA), copper-azole, ammoniac copper arsenate (ACZA), and amine/ammoniac copper quat are commercially used to treat wood to extend the service life of wood [5]. Some researchers used copper-containing chemicals to limit the photodegradation of wood and the influence of weathering factors [1,6–8]. Among them, chromate copper arsenate (CCA) has high resistance to leaching and has provided long-term protection against weathering, as well as erosion in service. Nevertheless, the increasing public concern about the hazard to the environment and humans of chromium and arsenic, with the result, this conventional wood preservative has been restricted in many countries and total ban in the European Union [9]. Therefore, the new trends in wood preservation focus on environmentally friendly products and sustainable resources using recycled material or by-products from other industries.

Many studies, natural resources have been used as raw materials or in combination with boron or copper salts to study the development of new preservation systems with good effect, workable economic, and friendly to the environmental [10–12]. Rosin is also a natural product. It was obtained from pines and some other plants. Rosin has good hydrophobic properties because its main component is abietic acid, a partially unsaturated compound with three fused six-membered rings and one carboxyl group. For many years, rosin was widely used as a sizing agent in the paper industry [13]. Besides, rosin-copper soaps obtained as dissolved in benzene or ethanol had used to impregnated into wood and the result showed that treated wood blocks have presented to be good effective against both termites and fungi and this approach is known to have allowed 20 years of unaltered wood protection from termite and fungal attack in ground contact in tropical grounds in Africa [14,15]. Moreover, our previous studies indicated that the rosin sizing agents had an obvious effect on the fixation of copper in wood and can reduce wood's tendency to absorb moisture, as well as enhance wood decay resistance after being treated with the rosin-copper/boron formulations [16–20]. However, to the best of our knowledge, there are no researches on the behavior of copper-rosin treated wood under weathering. Therefore, the aim of this study was to evaluate the changes in wood caused by weathering such as color stability, gloss, weight loss, compression strength, modulus of rupture (MOR), and modulus of elasticity (MOE) on wood impregnated with new rosin-copper preservatives after natural weathering exposure. These are the main criteria for the selection and design of wood for the next process as well as various usages.

2 Materials and Methods

2.1 Preparation of Wood Samples and Impregnation Solutions

Twelve-year-old Styrax wood (*Styrax tonkinensis* Piere) (a wood species with growth ring boundaries indistinct and density of about 410 kg/m^3) was selected by GB 1929 [21] from Hoa Binh, Viet Nam. Wood samples were prepared from untreated Styrax wood with four various dimensions. The sample of 20 × 20 × 20 mm was used for the mass-loss test, 30 × 20 × 20 mm for compression strength parallels to grain, 300 × 20 × 20 mm for bending test, and 145 × 50 × 5 mm for the color and gloss test (longitudinal, tangential, and radial, respectively). Defect-free samples were selected for the experiments. There are eight groups: one untreated group was used as a control, and the other seven groups were impregnated with rosin sizing agents alone or combined with copper sulfate. Each treatment group had 30 samples per type of test.

The rosin-copper formulations were prepared from 1%, 2%, or 4% anionic rosin emulsion sizing agent (provided by Guangxi Wuzhou Arakawa Chemical Industries Co., Ltd., China) and 3% copper sulfate ($CuSO_4 \cdot 5H_2O$), respectively. The other chemical reagents used in this study were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China and all were pure grade reagents.

2.2 Impregnation Process

Wood specimens were oven-dried to constant weight at 60 ± 2°C. Then the samples were impregnated using a full-cell pressure process at 0.1 MPa vacuum for one hour followed by 0.6 MPa pressure for one hour. After that, the samples were kept in the solutions for one hour at atmospheric pressure. The wood specimens were then removed from the treatment solution, wiped lightly to remove the rest of the solution from the wood surface, and weighed to determine retention for each treatment solution.

After treatment, the specimens were conditioned at laboratory temperature for air-dry for 4 weeks.

2.3 Weathering Exposure

The specimens were exposed to natural weathering conditions from the 1st of April, 2019 to the 31st of March, 2020. The weathering site was located at the Vietnam National University of Forestry in Ha Noi, Vietnam. The weather conditions for Ha Noi during the weathering period are shown in Table 1.

Table 1: Climate conditions of Ha Noi city during the weathering period

Year	2019									2020		
Month	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
Average temperature (°C)	27.5	28.3	31.6	31.6	30	29.5	26.7	23.5	19.6	19.6	19.7	23.2
Highest temperature (°C)	38	41.3	40.4	40.4	39.7	37.1	35.1	30.9	28.9	28.5	22.9	34.9
Lowest temperature (°C)	19.5	22	23.3	23.3	24.5	23	19.2	17.3	12.4	12.7	17.8	15.4
Total rainfall per month (mm)	166	97	97	97	489	114	105	44	4	157	28	180
Number of rainy days	15	19	11	11	20	10	10	6	5	13	11	19

Source: (IMHEN 2019) [22].

The exposure rack was positioned so that the exposed specimens were at a 45° angle facing south. The wood specimens were set outside for weathering exposure according to ASTM G7/G7M-13 (2013). The exposure period was 6 months and 12 months. The assessment of the weathered samples consisted of color, gloss measurement, mass loss, and some mechanical properties of the wood specimens before and after weathering.

2.4 Gloss Measurement

The gloss values of wood samples were measured using a Gloss checker (HORIBA IG-320, HORIBA. Ltd., Japan) according to ASTM D523-14 [23] and were measured according to the direction parallel to the wood grain. The measurement geometry was chosen from an incidence angle of 60°. The result was based on a specular gloss value of 91, which related to the perfect condition under analogous illumination and viewing conditions of black glass with a highly polished, plane surface.

2.5 Color Measurement

The color of wood samples was measured on the exposed wood surfaces before and after weathering and was performed *via* an NF–333 Spectrophotometer (Nippon Denshoku Industries Co. Ltd., Japan) with a standard measuring aperture of 4 mm diameter. The CIELAB system is characterized by three parameters, lightness (L*) and color coordinates (a* and b*). The values of these parameters for each sample were determined before and after weathering. The color change, ΔE* after each weathering period, was calculated following Eqs. (1) through (4),

$$\Delta L^* = L^*_f - L^*_i \quad (1)$$

$$\Delta a^* = a^*_f - a^*_i \quad (2)$$

$$\Delta b^* = b^*_f - b^*_i \quad (3)$$

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (4)$$

where ΔL*, Δa*, and Δb* are the changes between the initial (i) and final (f) values. The changes in L*, a*, and b* values contribute to the overall color change, ΔE*.

2.6 Mass Loss

The mass loss of all treated and untreated samples during wethering was calculated based on the initial (Wi) and the final (Wf) weathered weight.

$$\text{Mass loss } (\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (5)$$

Each of the 20 samples in all of the groups was weighed.

2.7 Mechanical Tests

The mechanical properties of both treated and untreated samples before and after weathering were performed by using an Instron Universal Testing Machine. Compression strength parallel to grain (CSPG) was conducted following GB/T 1935 [24]. Modulus of rupture (MOR) was done as per GB/T 1936.1 [25] and modulus of elasticity in bending (MOE) was tested according to GB/T 1936.2 [26].

At the end of experiments, moisture contents (W) of wood samples were tested per GB 1931-2009 [27] and the moisture contents of samples that deviated from 12% were then used to correct strength values (converted to 12% moisture content) using the following strength transformation equation:

$$\sigma_{12} = \sigma_w \times [1 + \alpha(W - 12)] \quad (6)$$

where σ_{12} = strength at 12% moisture content (N/mm^2), σ_w = strength at moisture content deviated from 12% (N/mm^2), α = constant value showing relationship between strength and moisture content (α = 0.05, 0.04, and 0.015 for CSPG, MOR, and MOE, respectively), W = moisture content during test (%).

2.8 Microscopic Observation

After weathering test, small specimens (1 cm × 1 cm × 1 mm) were cut with a razor blade from the untreated control and treated wood samples. The specimens were then attached to a metal stub with adhesive, dried under vacuum, and sputter-coated with a 20 nm layer of gold. After that, the specimens were observed with a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDX, FEI Quanta 200; USA) operating at an accelerating voltage of 20 kV. Random observations were performed on various positions of the wood to discover the presence of copper in the anatomical structure of the specimens. The elemental composition was examined by spot analysis using the energy dispersive X-ray analyzer combined with the scanning electron microscope.

2.9 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectroscopy experiments were carried out using an Agilent Cary 630 FTIR (Agilent Technologies, Inc., Danbury, CT, USA) equipped with a diamond ATR (attenuated total reflectance) module. FTIR measurements were carried out at the times when the critical color changes were observed to detect chemical changes on the components of the wood surface by outdoor degrading agents. FTIR spectrum presented is based on a recording of was scanned 32 times at a spectral resolution of 2 cm^{-1} in the wavenumbers ranging from 650 to 4000 cm^{-1}. Four analyses were performed at four locations per sample. The information from these spectra was extracted with Agilent MicroLab PC software from Agilent Technologies (USA).

2.10 Statistical Analysis

To determine the effects of wood preservatives on the properties of wood, the mean comparison of different formulations used in the color change, gloss and mechanical properties study has been analyzed by one-way ANOVA and homogeneous groups by using SPSS 25.0 statistical software package.

3 Results and Discussion

3.1 Mass Loss

The mass loss of wood samples impregnated with copper sulfate and rosin sizing agent, separately or in combination after natural weathering are provided in Fig. 1. The average mass loss of control wood blocks was 27.9% and 45.82% after 6 and 12 months of exposure, respectively. The samples impregnated with only rosin sizing agents had mass losses in the range of 21.81 to 22.86% and 35 to 36.84% after 6 months and 12 months of exposure. This could be due to the rosin sizing agent decreasing the moisture-absorbing tendency of wood helping hancing performance against attacks by biological agents, particularly fungal attacks [16]. The SEM images (Figs. 3b and 3d) also showed that many hyphae were detected in the cell lumen and surface of wood cell walls of the untreated control and rosin sizing agents treated samples were seriously destroyed by the fungi after weathering. Notably, when copper sulfate was added into rosin sizing agent solutions, the weight loss of styrax wood samples was less than 5% after natural weathering for 12 months, while no remarkable changes in weight loss values of wood could be observed between samples treated with any of the 3 concentrations of rosin sizing agent (1.0, 2.0, or 4.0%) (Fig. 1). However, wood blocks treated with copper alone presented a slightly higher average mass loss than the rosin-copper treated ones, this could be due to mass losses of copper treated samples were not only the result of biodegradation but the result of leaching, too [18]. The spot analysis using SEM-EDX also revealed that various spherical particles were detected in the cell lumen of the sample treated with copper alone before weathering (Fig. 3e) and these particles contained much higher Cu content and lower C content in comparison to that observed in the sample treated with rosin-copper (Fig. 3g). After weathering, these particles were still detected in the cell lumen (Fig. 3f), but they had an equivalent Cu content with that observed in rosin-copper ones (Fig. 3h). These results demonstrated that the rosin sizing agent had a certain effect on the limited leaching of copper by water, and thus that the rosin-copper formulations showed better fungal resistances than copper sulfate after natural weathering.

3.2 Color Stability

The color change was the most important factor in the weathering evaluation. Table 2 presents the L*, a*, and b* values for the untreated (control) and the impregnated samples before being exposed to natural weathering. In addition, the change in value for all three color parameters (ΔL*, Δa*, and Δb*) were illustrated, as well as the total color change (ΔE*) of the wood samples after 6 months and 12 months of natural weathering. Before weathering, the L*, a*, and b* values of the untreated (control) styrax wood samples were 86.35, 4.94, and 16.89, respectively. The L* values of the impregnated styrax wood samples changed from 75.56 to 83.18, the a* values changed from 1.06 to 8.76, and the b* values changed from 18.41 to 26.04. These results showed that styrax wood had a white, reddish, and yellowish color before exposure to natural weathering (Fig. 2). After being treated with rosin sizing agents, the color of samples became redder and more yellow, however, after being combined with copper sulfate, the treated wood surface changed greener and slightly darker than the others. This result was due to the presence of copper in the impregnation solution.

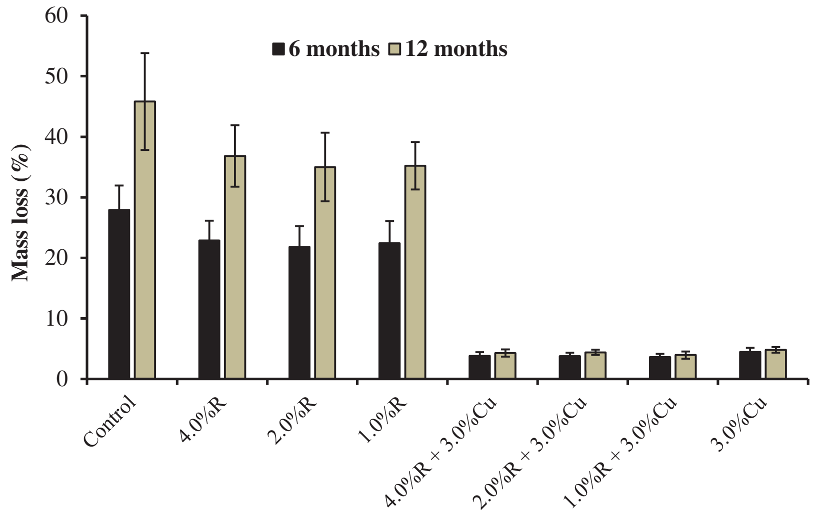

Figure 1: Mass loss of untreated controls and samples treated with rosin alone and in combination with copper after weathering (Cu: anhydrous copper sulfate and R: rosin sizing agent)

Table 2: Color change of wood treated with rosin-copper before and after natural weathering

Solutions and concentrations	Retention (kg/m^3)	Before natural weathering		
		L*	a*	b*
1.0%R	6.10 (0.48)	82.91 (2.53)^{d}	6.15 (1.51)^{d}	20.66 (2.12)^{c}
2.0%R	10.11 (1.27)	83.18 (1.81)^{d}	6.42 (1.28)^{d}	21.85 (2.16)^{d}
4.0%R	27.37 (1.58)	79.21 (2.14)^{c}	8.76 (0.92)^{e}	26.04 (1.99)^{e}
1.0%R + 3.0%Cu	28.15 (1.12)	75.56 (2.62)^{a}	4.51 (0.93)^{c}	21.02 (1.27)^{cd}
2.0%R + 3.0%Cu	35.68 (3.19)	80.13 (1.42)^{c}	1.06 (0.96)^{a}	18.48 (0.98)^{b}
4.0%R + 3.0%Cu	40.74 (4.46)	77.29 (2.48)^{b}	1.26 (0.77)^{a}	20.19 (1.41)^{c}
3.0%Cu	14.48 (2.34)	80.33 (0.98)^{c}	3.79 (0.59)^{b}	18.41 (0.6)^{b}
Control	–	86.35 (0.53)^{e}	4.94 (0.27)^{c}	16.89 (0.62)^{a}
Solutions and concentrations	After 6 months weathering			
	ΔL*	Δa*	Δb*	ΔE*
1.0%R	–27.41 (2.82)^{b}	–4.4 (1.21)^{b}	–14.75 (1.41)^{b}	31.54 (1.62)^{d}
2.0%R	–28.55 (1.82)^{ab}	–3.83 (0.25)^{b}	–14.82 (0.37)^{b}	32.41 (1.57)^{d}
4.0%R	–22.78 (2.67)^{d}	–7.00 (1.06)^{a}	–20.34 (2.34)^{a}	31.36 (3.39)^{d}
1.0%R + 3.0%Cu	–24.53 (2.68)^{cd}	–1.64 (0.78)^{d}	–12.73 (1.73)^{c}	27.78 (2.01)^{c}
2.0%R + 3.0%Cu	–25.46 (1.05)^{c}	2.41 (0.67)^{g}	–8.49 (0.99)^{e}	26.97 (0.97)^{bc}
4.0%R + 3.0%Cu	–23.64 (1.45)^{cd}	1.48 (0.98)^{f}	–10.97 (0.57)^{d}	26.19 (1.22)^{ab}
3.0%Cu	–23.65 (1.16)^{cd}	–0.46 (0.73)^{e}	–8.14 (0.97)^{e}	25.02 (1.38)^{a}
Control	–29.74 (1.53)^{a}	–2.99 (0.29)^{c}	–10.37 (0.86)^{d}	31.64 (1.54)^{d}

(Continued)

Table 2 (continued)

Solutions and concentrations	After 12 months weathering			
	ΔL^*	Δa^*	Δb^*	ΔE^*
1.0%R	–32.91 (3.10)[b]	–4.19 (1.71)[b]	–14.30 (2.42)[bc]	36.28 (2.37)[c]
2.0%R	–34.54 (2.21)[ab]	–4.48 (1.52)[b]	–15.76 (2.37)[b]	38.32 (2.34)[d]
4.0%R	–30.67 (3.05)[c]	–6.57 (1.06)[a]	–19.66 (2.10)[a]	37.11 (2.78)[cd]
1.0%R + 3.0%Cu	–29.07 (2.42)[c]	–2.22 (1.15)[c]	–13.96 (1.50)[c]	32.42 (1.69)[b]
2.0%R + 3.0%Cu	–30.55 (1.04)[c]	2.08 (0.52)[e]	–10.19 (0.88)[d]	32.29 (0.96)[b]
4.0%R + 3.0%Cu	–26.98 (2.00)[d]	1.38 (0.85)[e]	–12.89 (1.25)[c]	29.99 (1.45)[a]
3.0%Cu	–29.76 (0.99)[c]	–0.63 (0.68)[d]	–9.7 (0.71)[d]	31.33 (0.99)[ab]
Control	–36.01 (1.36)[a]	–2.37 (0.33)[c]	–9.41 (0.91)[d]	37.31 (1.48)[cd]

Note: Standard deviations are in brackets; Cu: anhydrous copper sulfate 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.

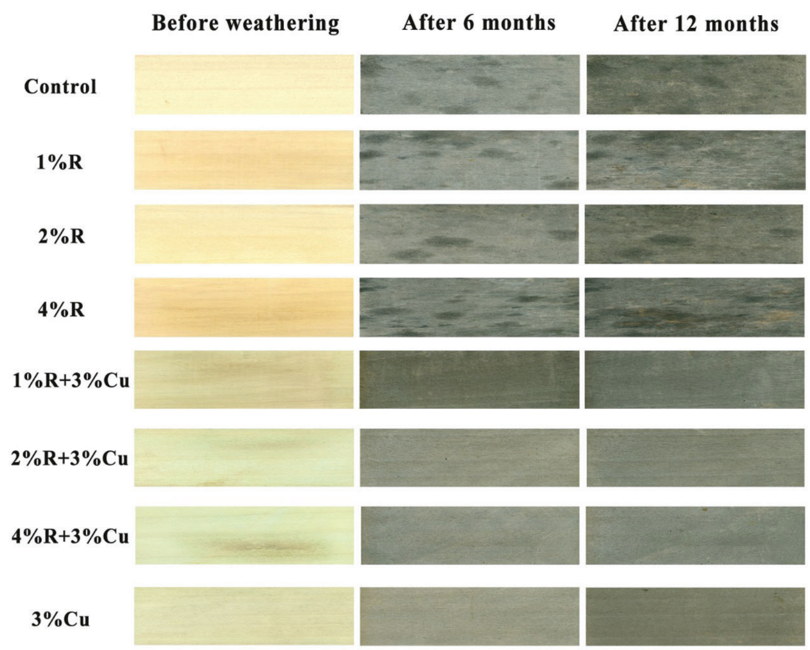

Figure 2: Images of untreated control and treated samples before and after weathering (Cu: anhydrous copper sulfate and R: rosin sizing agent)

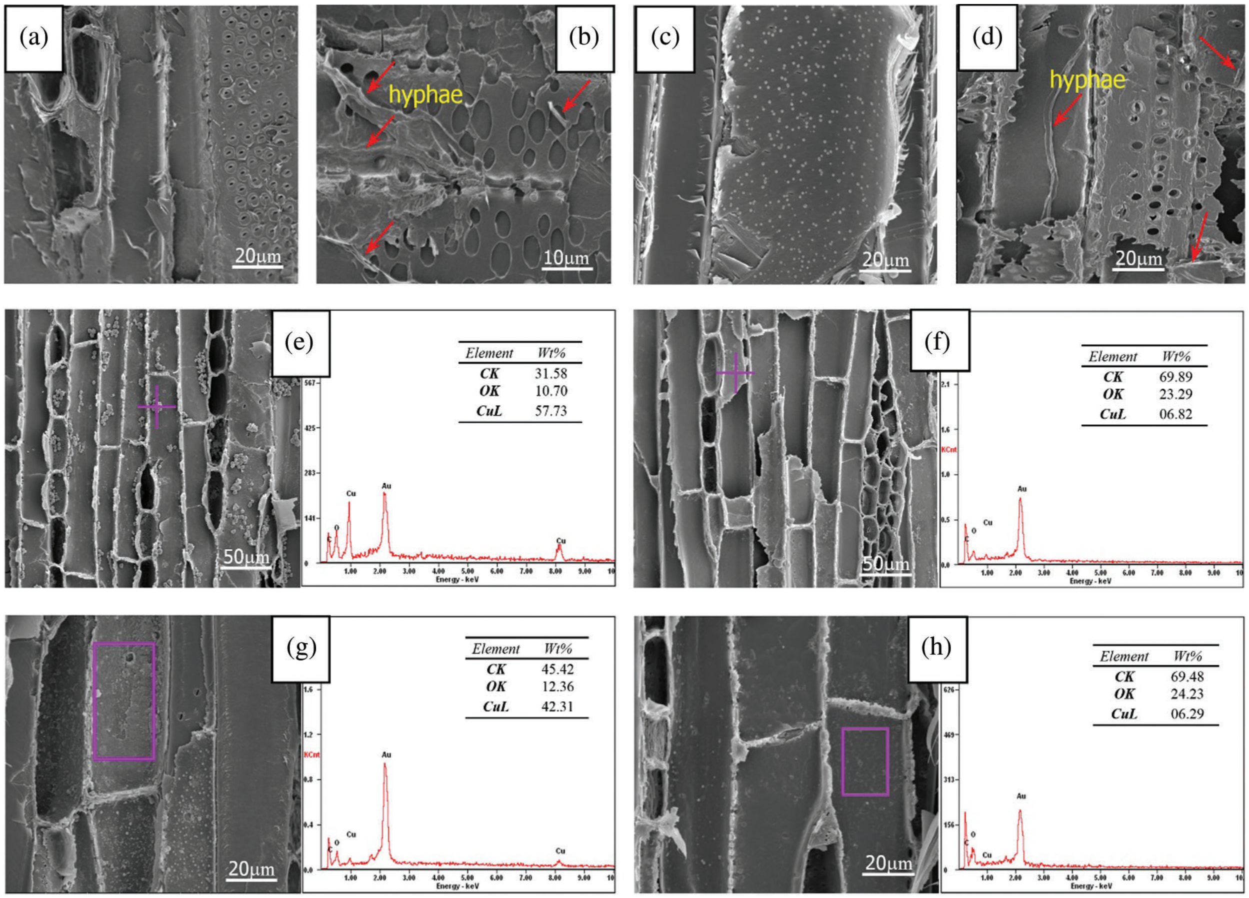

Figure 3: SEM images and corresponding spectrum of styrax samples treated with rosin-copper before (a,c, e,g) and after (b,d,f,h) 12 month weathering: untreated control (a,b); 1% Rosin treated sample (c,d); 3% $CuSO_4$ treated sample (e,f) and 2% Rosin + 3% $CuSO_4$ treated sample (g,h)

After 12 months of weathering exposure, the values of Δa* and Δb* were observed to have negative values in all untreated control and wood samples treated with the rosin sizing agent or copper sulfate alone. This presented that the styrax wood surface turned from red to green and tended to become bluer after weathering. However, the Δa* values were observed to have positive values in the samples treated with 2% and 4% rosin sizing agents combined with copper sulfate. In other words, the red tone of wood samples had not changed remarkably. This might be due to the modification of some chromophoric groups of lignin. The color change is ascribed to the carbonyl groups of the aldehydes, conjugated ketones, and quinines resulting from lignin and other compound modifications [5]. After the rosin-copper formulations impregnated into wood likely forms certain complexes with functional groups in wood, such as copper-lignin complexes, copper-cellulose complexes, crystalline or amorphous inorganic/organic copper compounds [5], and form an insoluble copper resinate compound [14]. These complexes can photostabilize wood and prevent the formation of carbonyl groups [28]. The ΔL* values were noted as the most sensitive parameter of the wood surface quality [7]. The negative lightness stability (ΔL*) values were found for both the untreated and treated samples, this indicated the styrax wood surface became darker after natural weathering exposure. The darkening of the wood might have been explained by the degradation of the lignins and other non-cellulosic polysaccharides [5,29]. In addition, the stabilization of the wood color in the visible region may have occurred from a reduction in lignin degradation, which was due to UV light irradiation [29]. The lowest values of ΔL* were observed for the untreated styrax wood after weathering. This may have been since untreated samples were influenced by other outdoor agents such as molds (Fig. 2). The total color change (ΔE*) of the untreated control was 37.31, while it ranged from 29.99 to 38.32 for the treated styrax samples after weathering. Moreover, one-way ANOVA analysis revealed that the ΔE* values of the rosin–copper formulations treated samples were significantly less than that of the untreated controls or wood samples treated with rosin sizing agent alone. This suggested that there is a positive contribution of rosin-copper to the color stability of wood after weathering. However, the concentration of rosin had no significant effect on the color stability of the wood.

3.3 Gloss

The results of gloss and gloss loss values of untreated controls and impregnated styrax samples before and after natural weathering are given in Table 3. Before natural weathering, the gloss values of untreated (control) wood samples were higher than that of the impregnated samples. The gloss value observed was 3.98 for the untreated (control) styrax samples, while the gloss values of all of the other impregnated styrax samples were between 2.70 and 3.64 before weathering. These results showed that Styrax wood after being treated with rosin sizing agents alone or combined with copper sulfate resulted in the decreased glossiness of wood surface. It can be explained that the impregnation process with the solutions might have increased the surface porosity and limited the glossiness to a definite point due to the absorption and dispersion of the reflected rays by salt crystals prominent in the large vessel lumens in the wide earlywood sections of the grains [30]. The lowest gloss value was observed in wood samples impregnated with copper sulfate before weathering. This was due to the presence of copper caused the treated wood surface to turn greener and darker than the others (Fig. 2), while glossy surfaces were obtained at a later time. This result is consistent with the suggestion of previous researches that wood treated with the copper-based formulation caused a high decrease in the glossiness of wood [7,8,31]. A preservative impregnation enhanced the gloss of Styrax wood by 15.1% after 6 months of natural weathering was found for copper sulfate treated samples, while the gloss of untreated and the other treated wood sample decreased from 2.8% to 15.2% after weathering. The reason for this observation may be due to the light absorption of chemicals [6]. However, after 12 months of natural weathering, the gloss values of all wood samples decreased by a considerable level. Untreated control and wood samples treated with rosin sizing agents alone exhibited higher gloss losses than the other wood samples in all the stages of natural weathering. The reason for these drastic gloss losses is that abrasion on the wood surfaces by fungi and insects, as well as the weathering conditions, along with erosion, also caused gloss degradation (Fig. 2). The highest gloss loss was observed to be 39.2% for wood samples impregnated with rosin sizing agents alone, the lowest gloss loss was obtained in wood samples impregnated with copper sulfate by 9.5% after 12 months of natural weathering. These results showed that the rosin-copper treatment could limit the gloss loss of wood under natural weathering. However, the rosin concentration had no significant impact on the gloss stability of the wood surface.

Table 3: Gloss change of wood treated with rosin-copper before and after natural weathering

Solutions and concentrations	Retention (kg/m^3)	Gloss value			Change (%)	
		Before weathering	After 6 months	After 12 months	After 6 months	After 12 months
1.0%R	6.10 (0.48)	3.64 (0.11)^{b}	3.42 (0.36)^{c}	2.34 (0.59)^{ab}	–6.1	–35.8
2.0%R	10.11 (1.27)	3.56 (0.33)^{b}	3.08 (0.25)^{bc}	2.16 (0.19)^{ab}	–11.3	–39.2
4.0%R	27.37 (1.58)	3.58 (0.42)^{b}	3.33 (0.81)^{c}	2.22 (0.36)^{ab}	–7.1	–38.0
1.0%R + 3.0%Cu	28.15 (1.12)	2.73 (0.48)^{a}	2.65 (0.44)^{a}	2.05 (0.13)^{a}	–2.9	–25.1
2.0%R + 3.0%Cu	35.68 (3.19)	2.92 (0.25)^{a}	2.82 (0.34)^{ab}	2.21(0.20)^{ab}	–3.3	–24.4

(Continued)

Table 3 (continued)

Solutions and concentrations	Retention (kg/m^3)	Gloss value			Change (%)	
		Before weathering	After 6 months	After 12 months	After 6 months	After 12 months
4.0%R + 3.0%Cu	40.74 (4.46)	2.89 (0.55)[a]	2.81 (0.29)[ab]	2.21 (0.10)[ab]	–2.8	–23.4
3.0%Cu	14.48 (2.34)	2.70 (0.26)[a]	3.11 (0.21)[bc]	2.44 (0.19)[bc]	15.1	–9.5
Control	–	3.98 (0.29)[c]	3.37 (0.27)[c]	2.66 (0.30)[c]	–15.2	–33.1

Note: Standard deviations are in brackets; R: rosin sizing agent and Cu: anhydrous copper sulfate. Means within a column followed by the different letters indicate a significantly different at 5% level of significance using the one-way ANOVA test.

3.4 FTIR Results

The FTIR spectra of untreated control and styrax wood treated with rosin-copper before and after natural weathering are represented in Fig. 4. There was a strong broad O-H stretching absorption band at 3300–4000 cm^{-1} and a C-H stretching at 2800–3000 cm^{-1} which are basic patterns of wood FTIR spectra. These bands did not significantly change during the weathering. However, in comparison with the untreated control, there is a decrease in the absorption peak of O-H and C-H of samples treated with rosin-copper solutions both before and after weathering. This means rosin-copper treatments could support the improvement of the hydrophobic performance of wood, dimensional stability and also help improve wood decay resistance [16,32,33].

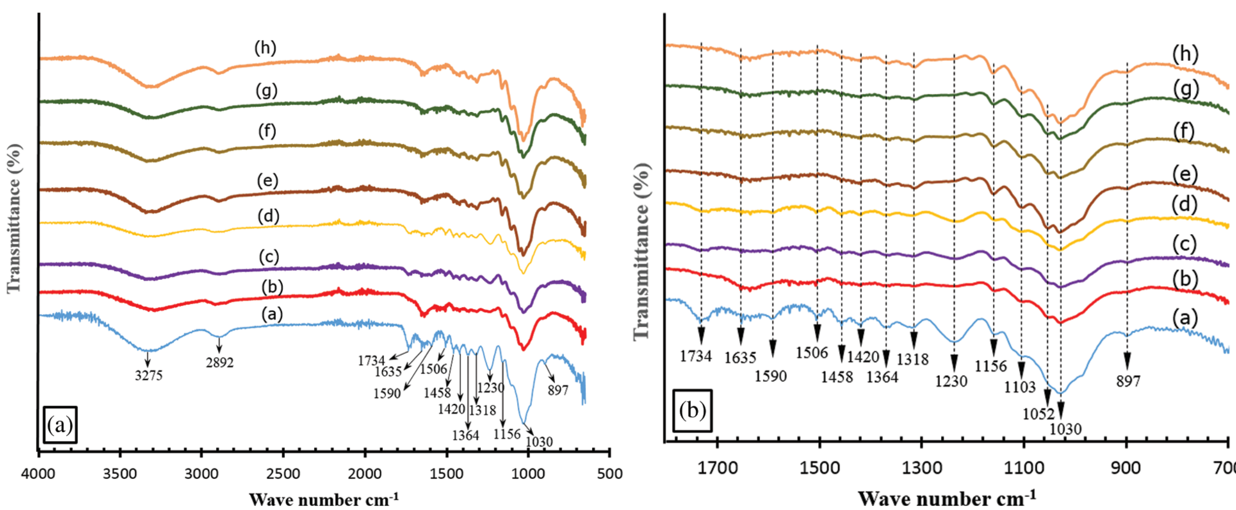

Figure 4: FTIR spectra of the exposed surface of styrax wood treated with rosin-based micronized-copper: untreated before (a) and after 12 month weathering (b), Cu treated before weathering (c), R+Cu treated before weathering (d), Cu treated and weathered 6 month (e), R+Cu treated and weathered 6 month (f), Cu treated and weathered 12 month (g), R+Cu treated and weathered 12 month (h)

After weathering, there are some significant changes of FTIR bands in the fingerprint region (Fig. 4B). It was observed that the peak intensity significantly decreased for the 1734 cm^{-1} band which belongs to the stretching of acetyl and carboxyl acid (hemicelluloses). This chemical change could be due to the degradation of acetyl groups [34] and leaching of the degraded carbonyl content or the copper ion to react with the hemicellulose on the surface of the wood [1]. However, it found that reduction for treated samples is less than for the untreated control. This suggested that rosin-copper treatments could limit the degradation of hemicellulose. The intensity of another band at 1635 cm^{-1} (belonging to absorbance peak –O–) was slightly modified and changes in the FTIR spectra around this wave number might be due to various moisture levels in the samples [35]. There is a significant decrease that can be observed at the 1590–1506 –1458–1230 cm^{-1} band regions on both untreated and treated samples after weathering. The peaks at 1590 cm^{-1} and 1506 cm^{-1} were assigned to the C=C aromatic skeletal vibration of lignin. The peak at 1458 cm^{-1} was assigned to the C-H deformation in lignin and the peak at 1230 cm^{-1} was assigned to C=O stretching vibration in lignin [1,36]. The same trend was observed for the band at 1420 cm^{-1}. After weathering, just a shoulder is observed on the FTIR spectrum. Notably, the specific lignin band at 1590, 1506 and 1230 cm^{-1} nearly disappeared for untreated controls after 12 months of weathering (Fig. 4B). The decrease of these absorption peaks is a clear indication of the decrease of lignin and other aromatic compounds on the surface of weathered wood [36,37]. Other bands at 1364, 1318, 1156, 1052, 1030, and 897 cm^{-1} are mainly associated with carbohydrates mostly cellulose. These bands only were modified slightly for rosin-copper treated samples after natural weathering, which means that the total surface degradation of the cellulose is not reached [37]. A similar result can be found in the literature [2]. However, there is a significant decrease in the absorption peak of these bands for untreated control after weathering. These results suggested that rosin-copper formulations could reduce the degradation of components of wood by weathering factors.

3.5 Compression Strength Parallels to Grain (CSPG) Result

The CSPG values of wood specimens before and after weathering are presented in Table 4. Before weathering, CSPG of wood specimens impregnated to copper sulfate or rosin sizing agents alone reduced slightly compared with the untreated controls. This result corresponded well with the reported results by Yildiz et al. [38]. However, the CSPG of wood specimens impregnated to rosin-copper formulations increased range in 6.3%–10% compared with the untreated controls. This could be due to the formation of insoluble copper resinate compounds as rosin reacting with copper (Fig. 3g) [14,18], which greatly enhances their lateral stability [39]. This had been proved in the previous study [33].

Table 4: Compression strength parallel to grain of styrax wood treated with rosin-copper before and after natural weathering

Treatments	Retention (Kg/m^3)	Compression strength, MPa, at 12% MC			Change (%)		
		Before weathering	After 6 months	After 12 months	Before weathering	After 6 months	After 12 months
1.0%R	6.24 (0.43)	35.20 (2.72)[ab]	17.94 (1.31)[a]	14.16 (1.66)[b]	0.5	–49.0	–59.8
2.0%R	12.91 (0.99)	34.67 (5.01)[a]	18.48 (2.95)[a]	12.85 (2.18)[b]	–1.0	–46.7	–62.9
4.0%R	24.96 (1.66)	34.67 (5.44)[a]	19.99 (3.04)[a]	13.38 (1.60)[b]	–1.0	–42.4	–61.4
3.0%Cu	20.65 (1.45)	34.77 (3.03)[a]	33.84 (5.13)[b]	33.30 (3.20)[c]	–0.7	–2.7	–4.2
1.0%R + 3.0%Cu	25.23 (1.35)	38.52 (2.91)[b]	36.70 (3.22)[b]	36.62 (4.23)[d]	9.9	–4.7	–4.9

(Continued)

Table 4 (continued)

Treatments	Retention (Kg/m^3)	Compression strength, MPa, at 12% MC			Change (%)		
		Before weathering	After 6 months	After 12 months	Before weathering	After 6 months	After 12 months
2.0%R + 3.0%Cu	33.12 (1.86)	37.58 (3.31)^{ab}	34.98 (2.93)^{b}	33.91 (4.11)^{c}	7.3	–6.9	–9.8
4.0%R + 3.0%Cu	42.12 (2.72)	37.23 (2.59)^{ab}	36.40 (3.96)^{b}	34.16 (2.76)^{cd}	6.3	–2.2	–8.2
Control	–	35.03 (3.28)^{ab}	17.12 (2.89)^{a}	9.46 (0.99)^{a}	–	–51.1	–73.0

Note: Standard deviations are in brackets; Cu: anhydrous copper sulfate 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.

The compression strength of all samples decreased after being natural weathering. However, the reduction of CSPG of wood samples treated with rosin-copper solutions exhibited lower more than that of the untreated control and wood samples treated with rosin sizing agents alone in all the stages of natural weathering. This could be seen clearly in the result of the One-way ANOVA test (Table 4). Weathering caused a reduction in compression strength of untreated control as 51% and 73%, whilst for samples treated with rosin sizing agents alone range in 42%–49% and 61%–63% after 6-month and 12-month exposure, respectively. However, after combination with copper sulfate, the CSPG of samples treated with rosin-copper formulations only decreased by 2%–7% and 5%–10%, and the samples treated with copper sulfate alone caused losses of compression strength approximately 3% and 5% after 6-month and 12-month exposure, respectively. The results showed that the rosin-copper treated samples maintained their compression strength at a much higher level after weathering than did the untreated control or rosin sizing agents treated ones. This was due to the untreated control and rosin sizing agents treated samples were more erosion by fungi and UV degradation (Fig. 2), hence they showed a maximum decrease in compression strength. The SEM micrographs also showed that wood cell walls of the untreated control and rosin sizing agents treated samples were seriously destroyed by the fungi after weathering (Figs. 3b and 3d). However, in the microscopic observation of the wood blocks treated with copper alone (Fig. 3f) or with rosin-copper (Fig. 3h) after weathering, the surface of the wood cell wall was still smooth, not changed, and mycelium was not also detected in the cell lumen. This result corresponded well with the aforementioned results of mass loss and color change. However, there were no significant differences in the CSPG between samples treated with copper sulfate alone and samples treated with rosin-copper solutions, and the concentration of rosin used also did not affect the CSPG of Styrax wood before and after weathering.

3.6 Bending Results

The effect of weathering on the modulus of rupture (MOR) and modulus of elasticity (MOE) in bending of wood is an important parameter determining the performance of the treated wood to outdoor use. Table 5 summarized the MOR and MOE values of treated wood samples before and after 6 and 12 months of natural weathering. It can see that rosin-copper treatment caused a decrease in MOR of styrax wood samples before weathering, while it slightly increased or did not affect on MOE of styrax wood samples. Namely, reductions in MOR of samples treated with rosin alone were 1.6%–2.7% and after combination with copper sulfate were in the range 7.4%–8.4% compared to untreated controls. The MOE increased by 0.4%–2.5% for samples treated with rosin alone but slightly decreased by 0.5%–0.8% for samples treated with rosin-copper solutions. This result is in congruence with the results reported in previous research [33]. However, analysis of variance indicated that there is no significant effect of rosin-copper treatment on the bending strength of styrax wood.

Table 5: Average values of MOR and MOE of wood treated with rosin-copper before and after natural weathering

Treatments	Retention (Kg/m^3)	MOR at 12% MC (MPa)			MOE at 12% MC (MPa)			Change MOR (%)			Change MOE (%)		
		Before	6-month	12-month	Before	6-month	12-month	Before	6-month	12-month	Before	6-month	12-month
3.0%Cu	15.23 (0.23)	70.52 (3.6)^{a}	68.07 (5.48)^{b}	66.84 (2.64)^{c}	7340 (491)^{a}	7075 (241)^{d}	6972 (476)^{c}	–8.0	–3.5	–5.2	–0.5	–3.6	–5.0
1.0%R	5.36 (0.23)	75.11 (4.98)^{a}	65.39 (7.69)^{b}	59.71 (4.55)^{b}	7407 (752)^{a}	6120 (495)^{b}	5704 (408)^{b}	–2.0	–12.9	–20.5	0.4	–17.4	–23.0
2.0%R	11.72 (0.65)	74.56 (6.37)^{a}	64.62 (2.64)^{b}	59.50 (4.34)^{b}	7563 (831)^{a}	6344(295)^{bc}	5857 (441)^{b}	–2.7	–13.3	–20.2	2.5	–16.1	–22.5
4.0%R	20.72 (1.16)	75.43 (7.78)^{a}	65.52 (2.37)^{b}	60.04 (3.51)^{b}	7503 (309)^{a}	6316 (747)^{bc}	5821 (619)^{b}	–1.6	–13.1	–20.4	1.7	–15.8	–22.4
1.0%R + 3.0%Cu	20.58 (1.90)	70.86 (3.92)^{a}	68.31 (3.72)^{b}	66.72 (7.69)^{c}	7387 (483)^{a}	7037 (707)^{cd}	6948 (282)^{c}	–7.5	–3.6	–5.8	0.1	–4.7	–5.9
2.0%R + 3.0%Cu	26.14 (1.23)	70.99 (4.47)^{a}	68.35 (4.13)^{b}	67.21 (6.86)^{c}	7332 (801)^{a}	6946 (362)^{cd}	6877 (320)^{c}	–7.4	–3.7	–5.3	–0.7	–5.3	–6.2
4.0%R + 3.0%Cu	40.22 (1.14)	70.19 (3.41)^{a}	68.02 (5.96)^{b}	66.06 (5.40)^{c}	7323 (632)^{a}	6925 (594)^{cd}	6856 (534)^{c}	–8.4	–3.1	–5.9	–0.8	–5.4	–6.4
Control	0.00	76.63 (5.34)^{a}	36.87 (4.08)^{a}	26.39 (3.52)^{a}	7380 (687)^{a}	4085 (488)^{a}	3797 (340)^{a}	–	–51.9	–65.6	–	–43.8	–48.5

Note: Standard deviations are in brackets; Cu: anhydrous copper sulfate 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.

After weathering, MOR and MOE of samples were reduced for both treated and untreated control samples. Weathering caused a reduction in MOR as 51.9% and 65.6% and decrease ratio in MOE as 43.8% and 48.5% for untreated control after 6-month and 12-month exposure, respectively. However, it found that reduction in MOR is the range in 12.9%–13.3% and 20.2%–20.5% for samples treated with rosin sizing agents alone, 3.1%–3.7% and 5.3%–5.9% for samples treated with rosin-copper formulations, 3.5% and 5.2% for copper treated samples after 6-month and 12-month exposure, respectively. MOE decreased at a rate of 15.8%–17.4% and 22.4%–23% for samples treated with rosin sizing agents alone, 4.7%–5.4% and 5.9%–6.4% for samples treated with rosin-copper formulations, 3.6% and 5.0% for copper treated samples after 6-month and 12-month exposure, respectively. It clearly showed that MOR and MOE of copper alone or rosin-coper treated samples after weathering did not specifically change from the un-weathered copper alone or rosin-coper treated ones, however untreated controls or only rosin treated samples after weathering significantly reduced from the un-weathered ones. This could be attributed to the copper-based treatments reducing the delignification of wood [28] and enhancing against attack by microorganisms during the weathering exposure [16,18]. It was reported that the reductions in MOR and MOE after natural weathering to the severe attack of microorganisms and light-induced depolymerization of lignin and cell wall components and breakdown of wood microstructure [40]. This result corresponded well with the aforementioned results of mass loss and color change, as well as in the microscopic observation. The one-way ANOVA result also showed that there was a statistical difference in MOR and MOE values between untreated control and all treated samples in all the stages of natural weathering. However, no statistical difference was detected between samples treated with rosin sizing agents only and samples treated with copper sulfate only or the rosin-copper solutions after 6 months of weathering. The data in Table 5 also indicates that the concentration of rosin applied did not have effect in MOR and MOE of wood samples treated with rosin sizing agents only or plus with copper sulfate.

The result suggested styrax wood after being treated with rosin-copper formulations enhanced wood samples' resistance against weathering factors.

4 Conclusions

The influence of natural weathering on some surface characteristics and mechanical properties of styrax wood treated with rosin-copper preservatives were investigated.

The combinations of rosin sizing agent solutions and copper sulfate provided lower color changes and improved gloss of wood than the untreated control after weathering.

The FTIR revealed that rosin-copper treatments slightly decreased the intensities of acetyl groups and lignin, but carbohydrates seemed to no changes after 12 months of natural weathering.

After 12 months of natural weathering, mass loss of all rosin-copper treated samples was less than 5%, while no remarkable changes in weight loss values of wood samples treated with any of the 3 concentrations of rosin sizing agent.

Before weathering, all rosin-copper treatments increased the CSPG compared to control, but MOR and MOE of treated samples were slightly lower than those for untreated control. Natural weathering factors caused a decrease in all strength properties of untreated and treated samples compared to initial values. However, the reduction rate in CSPG, MOR and MOE for rosin-copper treated samples was lower than that of the untreated control, only by a maximum of 10%, 6% and 6.5%, respectively, while for untreated control was 73%, 65% and 49% after 12 months of weathering. The concentration of rosin used did not also affect CSPG, MOR and MOE of wood samples treated with rosin alone or in combination with copper.

The SEM observation and EDX analysis confirmed that rosin-copper formulation had a certain effect on the reduce the hazard of the copper preservative leaching into the environment, while also enhancing more resistance against weathering factors and other biotic factors.

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