EFFECTS OF WATER-BORNE ROSIN ON THE FIXATION AND DECAY RESISTANCE OF COPPER-BASED PRESERVATIVE TREATED WOOD

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A rosin sizing agent designed to impregnate wood and immobilize copper in wood cells for protection against decay was investigated. Poplar (*Populus ussuriensis*) wood was impregnated with combinations of 3% $CuSO_4$ solution and 1.0%, 2.0%, or 4.0% rosin sizing agent. The decay resistance of treated wood blocks was measured by a soil-block culture method. After a 12-week decay test, the weight losses of untreated control blocks were 70.45% by *Trametes versicolor* and 61.84% by *Gloeophyllum trabeum*. The wood decay resistance was also slightly improved by the treatment with only the rosin sizing agent. However, after being treated with the rosin sizing agent and $CuSO_4$, the wood had great decay resistance. The average weight losses of the samples degraded by fungi were less than 4%. Notably, the leached wood blocks had a weight loss of less than 3%. After leaching, the copper content in the leachates was analyzed by atomic absorption spectroscopy (AAS). Results showed that the amount of copper ions released from the samples treated with the copper-rosin solutions was half those from the samples treated with copper alone. Scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) proved that the copper element was still in the cell lumens of leached wood blocks, which is consistent with the results of AAS analysis. This signifies that the rosin sizing agent is very helpful to fix the copper preservative in wood.

Keywords: Rosin; Fixation; Decay resistance; Copper sulfate; Wood preservative

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INTRODUCTION

Copper compounds are known to have wood protection capacities and have been used for this purpose for more than 200 years. The efficacy of copper sulfate against wood decay due to fungi, insects, and marine borers was established in wood products from the 1970s and 1980s (Freeman and McIntyre 2008; Ngoc 2006). However, copper itself cannot ensure sufficient protection against wood destroying organisms because it is easily lost from treated wood (Ruddick 2000). In order to overcome this problem, copper usually has been combined with other compounds such as sodium fluoride (NaF), sodium hydroxide (NaOH), arsenic (As), chromium (Cr), borate, *etc.* Among these compounds, chromate copper arsenate (CCA) has been used extensively for wood preservation for the longest. Nevertheless, recognition of the risks to human's health and potential environmental damage has prompted changes in the types of preservatives used commercially in recent years. In particular, CCA was completely banned in the European Union and limited to nonresidential uses in the United States (Townsend and Solo-Gabriele 2006). This has stimulated the wood preserving industry to create new wood preservatives to minimize the environmental impact of treated wood.

Hence, current research has been focused on the development of more environmentally friendly, alternative wood preservatives to CCA. For example, arsenic/ chromium-free alternatives based on copper compounds, such as copper azole (CA) and ammoniacal copper quaternary (ACQ) have been introduced as alternative chemicals, and they have become a predominant choice worldwide in today's wood preservation systems (Nicholas and Schultz 1995; Nicholas and Schultz 1997). Subsequently, water-borne micronized copper formulations such as micronized copper azole and micronized copper quat also have come into use (McIntyre and Freeman 2008). However, the cost of these biocides has been much higher in comparison to the CCA.

Several different methods have been researched to decrease copper leaching from wood, such as combined wood impregnation processes, including impregnation with a copper-based, chromium-free wood preservative and subsequent impregnation with a hydrophobic product (Treu *et al.* 2011), incorporating additives into the preservative formulations to limit copper migration (MitsuhashiGonzalez 2007) and combining copper with other co-biocides, such as quaternary ammonium compounds, azoles, octanoic acid, amine, and boron to form an insoluble complex (Chen 2011; Humar et al. 2005; Humar et al. 2007; Zhang and Kamdem 2000). Some natural resources, such as the industrial waste enzymatic-hydrolyzed okara, have been used to enhance the fixation of antifungal salts in wood structures (Ahn *et al.* 2010; Kim *et al.* 2011), and tannins were also combined with copper and/or boron salts to formulate a new wood preservative system that showed good efficacy against fungal decay (Laks *et al.* 1998; Tondi *et al.* 2012). Other studies used soy protein products or commercial extracts as raw materials in their preservative formulations for the fixation of copper (Sen *et al.* 2009; Yang *et al.* 2006). However, such renewable resources are difficult to implement as fixatives in newly developed preservative systems because of their high cost and rarity.

Rosin, which comes from softwood, is abundant, natural, and renewable. It has a suitable hydrophobic character and affinity for wood. Over the years, its main widespread application has been in the paper industry as a sizing agent (Yao and Zheng 2000). Different chemical mechanisms between copper, rosin, and wood constituents have also been investigated (Pizzi 1993a). The copper-rosin soaps obtained when dissolved in a solvent (ethanol) have also been impregnated into wood (Pizzi 1993b), and the copper-rosin soaps were shown to be extremely efficient towards both fungi (unsterile soil bed test) and termites (field test). In another study, the use of non-solvent rosin-copper formulations to impregnate wood has also been proposed (Roussel *et al.* 2000) and treated wood blocks have shown good performance when leached, but a double impregnation system was required. In addition, earlier investigations showed that a rosin sizing agent can decrease the moisture absorbing tendency of wood and also help improve wood decay resistance (Li *et al.* 2009, 2011). Therefore, this study aims to investigate the effect of rosin size on copper fixation to develop new formulations for wood preservation and determine the efficacy of copper-rosin preservatives against fungal decay.

EXPERIMENTAL

Materials

The anion 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 treat wood at three concentrations (1.0, 2.0, and 4.0%). The analytical copper sulfate ($CuSO_4$: Cu) was used as preservative salts to protect wood against fungal decay in only one concentration of 3%. All of the other chemical reagents used in this work were provided by Tianjin Kermel Chemical Reagent Co., Ltd. and were all pure grade reagents.

Preparation of Test Samples

The wood samples were taken from poplar trees (*Populus ussuriensis* Komarov) at 15 years of age and were selected according to GB 1929-91. Wood specimens were cut from untreated poplar sapwood into block dimensions 20 x 20 x 20 mm. Defect-free cubes were selected for the tests. The weight differences of the chosen blocks could not exceed 0.5 g. Feeder strips were also prepared from poplar sapwood. One feeder strip (22 mm x 22 mm x 3 mm (longitudinal direction)) was needed for each cube in a culture bottle.

Impregnation Method

Before treatment, all blocks were oven-dried at 103 °C to a constant weight (the nearest 0.01 g) and recorded as W_1. After drying, the blocks for each retention group were placed in a suitable beaker and weighed down to prevent eventual floating during treatment. The process was performed in a small-scale impregnation container under a vacuum of 0.01 MPa for 30 minutes followed by injection of the preservative mixture and then brought back to atmospheric pressure.

After the blocks were completely saturated, they were individually removed from the solution and lightly blotted with absorbent paper to remove the excess preservative solution and immediately weighed to the nearest 0.01 g to ascertain 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 retention, the treated samples were air-dried for 48 hours, 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 treatability of each preservative formulation.

Leaching

A leaching test was performed according to AWPA E11 (American Wood Preservers' Association 2007 – Method of Determining the Leachability of Wood Preservatives).

Twelve blocks of a given retention group were placed equally on stainless steel in 1000 mL beakers. They were weighed down in each beaker and completely submerged with 50 mL of distilled water for each block. Then the beakers containing the blocks covered with water were placed into a vacuum desiccator. A vacuum process of 100 mm of mercury or less was adopted for one-half hour or until air bubbles ceased to escape from the submerged blocks. Then the vacuum was broken to allow water impregnation of the blocks, and the weights were removed from the blocks. After 6, 24, and 48 hours and thereafter at 48-hour intervals for 14 days, the leachates were removed from the beaker and kept for copper analysis. The amount of leachate was replaced by an equal amount of fresh distilled water.

Analysis of Copper

In order to measure the amount of copper ions leached from the treated wood blocks, the leachates were analyzed according to AWPA Standard A11-93 by using an atomic absorption spectroscopy (AAS) analyzer.

Decay Test

Wood blocks were tested to evaluate their resistance against biological attack according to Chinese standard LY/T 1283-1998. The white-rot fungi *Trametes versicolor* and brown-rot fungi *Gloeophyllum trabeum* were used as test fungi. Soil culture bottles with feeder strips on the soil surface were inoculated with fungus cultured on potato dextrose agar.

After the feeder strips were covered with fungal mycelia, sterilized wood blocks were placed onto the feeder strip. The soil-block culture was incubated in a temperature and humidity-controlled chamber at 28 °C and 75% RH for 12 weeks. After exposure to the fungi, the blocks were removed from the decay chambers, gently cleaned to remove the mycelium, dried at 103 °C until constant weight was obtained, and weighed to determine weight loss.

Microscopic Observation by SEM-EDX

After the decay test of wood blocks was completed, the wood blocks were sliced into thin samples using a razor blade. The samples were mounted on a metal stub and were sputter-coated with a thin layer (approximately 20 nm thick) of gold. The specimens were then observed with a scanning electron microscope (SEM, FEI Quanta 200; USA). Random observations were made on different structures to identify the existence of copper in the anatomical structure of the specimens. The element composition was determined by regional analysis using an energy dispersive X-ray spectrometer (EDX) combined with the scanning electron microscope.

RESULTS AND DISCUSSION

Retention Results

Retention levels of poplar wood samples treated with copper-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 treating solutions in poplar wood, including both rosin alone and in combination with copper, were relatively uniform. The actual retentions of the copper-rosin preservatives were very close to theory retention, namely above 85%. Results indicated that the concentration of the solutions considered using the impregnation method described did not influence the penetration of the preservative complexes into the wood blocks.

There were slight differences in the treatability of the three rosin formulations (Table 1). The actual percent retention of preservative solution-containing rosin only or containing copper-rosin decreased from 98.22 to 85.33% and from 98.38 to 89.66%, respectively, with the increase in concentration of rosin from 1.0 to 4.0% in the impregnation solution. An explanation for this would be that the increase of rosin concentration, which leads to increase in uptake, 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 actual retention of preservatives. However, this decrease was not important, and the best retention was obtained with 1% rosin size and 3% added copper sulfate.

Table 1. Retention Levels and Treatability of Wood Samples Treated with Solutions

Abbreviation	Solution and Concentrations	Theory Retention (kg/m^3)	Actual Retention (kg/m^3)	Treatability [a] (%)
1	1% Rosin + 3% $CuSO_4$	33.95 (0.93)[b]	33.48 (1.66)	98.38 (2.32)
2	2% Rosin + 3% $CuSO_4$	41.61 (1.69)	39.30 (2.07)	94.41 (2.17)
3	4% Rosin + 3% $CuSO_4$	58.32 (1.68)	52.29 (1.97)	89.66 (2.52)
4	3% $CuSO_4$	26.06 (1.26)	25.05 (2.14)	96.01 (4.49)
5	1% Rosin	7.9 (0.32)	7.75 (0.52)	98.22 (6.34)
6	2% Rosin	15.83 (0.94)	15.32 (1.32)	96.91 (7.34)
7	4%Rosin	31.72 (0.39)	27.06 (1.34)	85.33 (6.23)

[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.

Leaching

The analyzed results of copper ions released from blocks treated with the copper-rosin solutions and those treated with the copper sulfate solution alone taken at different time intervals are presented in Fig. 1. A significant reduction of copper ions leaching from wood samples treated with the copper-rosin solutions was observed. For all samples, the unfixed copper rapidly leached from wood during the first stages of the leaching process, and decreased significantly over time. However, the leaching of copper occurred much more slowly when wood samples were treated with rosin-copper solutions. This is probably attributable to the presence of rosin. After having penetrated into the wood blocks, the rosin molecules present in the cell lumen either interacted with copper to form an insoluble copper resinate compound (Pizzi 1993a) or were in the form of an adhesive film to cover the copper crystals, which could be proved by SEM-EDX analysis. During the leaching process, the rosin acted as a barrier that slowed copper release from deep inside the samples.

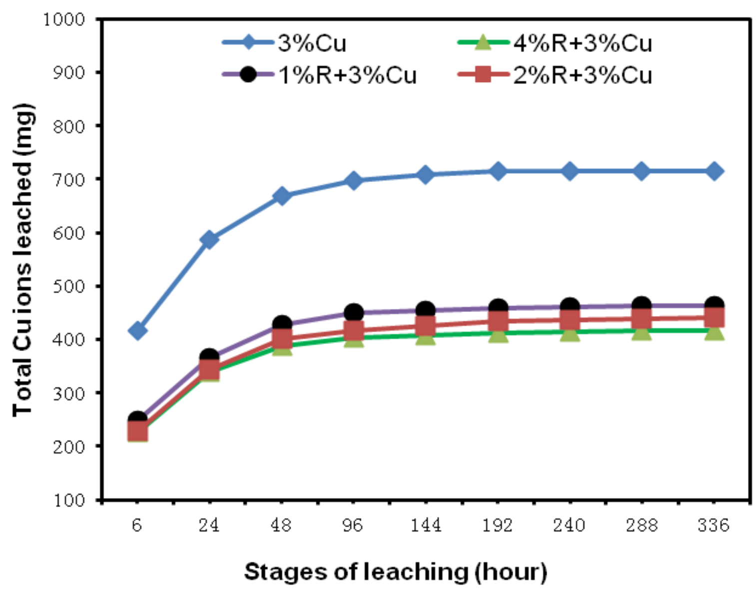

Fig. 1. Copper ions released from treated wood specimens at different time intervals.
Cu: copper sulfate ($CuSO_4$), R: rosin sizing agent

There was a large amount of copper ions that leached out from wood samples treated with copper sulfate alone. After 9 leaching cycles, 715.49 mg of copper was leached out from the samples, which represented 69.3% of the copper impregnated in the wood blocks, which is comparable with the results reported by Mourant *et al.* (2009) and Humar *et al.* (2005). However, due to the application of rosins in the present investigations, copper ion leaching was effectively reduced, particularly in the first stage of the process (Fig. 1). The total amount of copper ions released from the samples treated with the copper-rosin solutions was two times less than those from the samples treated with only copper sulfate. The treatments with copper-rosin showed that content of Cu ions leaching slightly decreased with the increase of rosin concentration in the impregnation mixture. This would be explained that when wood samples were impregnated with increasing concentration of rosin, a greater amount of rosin ended up on the surface of the treated wood, which resulted in the reduction of the copper ion diffusion from wood during leaching of the samples.

The results suggested that addition of rosin had a significant effect on the fixation of copper in wood, but the concentrations used in this work did not show a difference in the size of the effect.

Decay Resistance

The results from the decay test are shown in Table 2. The weight losses of the control wood blocks against *Trametes versicolor* and *Gloeophyllum trabeum* were 70.45% and 61.84%, respectively. The unleached wood blocks treated with copper alone exhibited approximately 4% or less weight loss for both test fungi. This result was in agreement with that reported. However, a severe weight loss (approximately 40%) was found for the leached wood samples treated with only copper.

Table 2. Weight Loss (%) of Samples Exposed to White Rot Fungus *Trametes versicolor* and *Gloeophyllum trabeum*

Abbreviation	Solution and Concentrations	Weight loss (%)			
		Gloeophyllum trabeum		*Trametes versicolor*	
		Unleached	Leached	Unleached	Leached
1	1% Rosin + 3% $CuSO_4$	3.14 (0.61)[a]	2.24 (0.86)	3.6 (0.63)	1.93 (0.47)
2	2% Rosin + 3% $CuSO_4$	3.16 (0.75)	1.24 (0.47)	3.26 (1.04)	2.11 (0.76)
3	4% Rosin + 3% $CuSO_4$	3.43 (0.73)	1.46 (0.57)	3.34 (1.06)	2.31 (0.68)
4	3% $CuSO_4$	3.04 (0.62)	34.14 (3.03)	2.66 (0.85)	39.12(3.23)
5	1% Rosin	48.46 (2.62)	51.04 (3.54)	51.32 (0.85)	54.98 (2.57)
6	2% Rosin	49.22 (3.32)	52.94 (5.06)	52.79 (1.44)	55.92 (2.05)
7	4%Rosin	49.25 (4.16)	51.45 (1.96)	51.25 (3.26)	54.45 (3.34)
8	Control	61.84 (5.68)	-	70.45 (4.94)	-

[a] All results are means of 6 samples. Standard deviations are in brackets.

As shown in Table 2, the samples impregnated with only rosin sizing agents and leached had weight losses in the range of 48 to 55%, which was much lower than those of the untreated control samples. Also, no remarkable changes in weight loss values of woods could be observed between poplar samples treated with any of the 3 concentrations of rosin (1.0, 2.0, or 4.0%). The differences between the weight losses after decay of the leached and unleached samples were not so pronounced in the rosin size samples as for the copper samples. This signifies that the rosin sizing agent itself also has poor performance against fungal wood decay because of its water repellency and inherent decay resistance rather than general toxicity (Eberhardt *et al.* 1994). This result was in accordance with that reported in previous research (Li *et al.* 2011).

However, the samples treated with copper-rosin formulations showed good decay resistance against both *Trametes versicolor* and *Gloeophyllum trabeum*. The average weight loss of the samples degraded by fungi was in a range of 1.24% to 3.46% after being incubated for 12 weeks. Most of the leached wood blocks treated with copper-rosin formulations showed less than approximately 3% weight loss and were not entirely covered by mycelium of both test fungi. In some cases, the unleached specimens presented a slightly higher average mass loss than the leached ones, which means that mass losses of unleached specimens were not only the result of fungal decay, but the result of leaching, too (Humar *et al.* 2007). When unleached specimens are exposed to fungi, moisture content of the wood increases and the unfixed copper will diffuse from specimens into soil culture resulting in mass losses, which are not a result of fungal action but of copper sulfate (Goodell *et al.* 1995). And when specimens are leached prior to fungal exposure, the unfixed copper is removed from wood during the leaching procedure. Thus, detected mass losses are a result of fungal decay only.

No significant differences in performance against wood decaying fungi were found between copper-rosin formulations. All wood samples containing copper-rosin gave a better performance against fungal decay than those only containing copper after leaching. Therefore, the use of rosin size as fixed agents may reduce environmental impact of wood treated with copper-based preservatives.

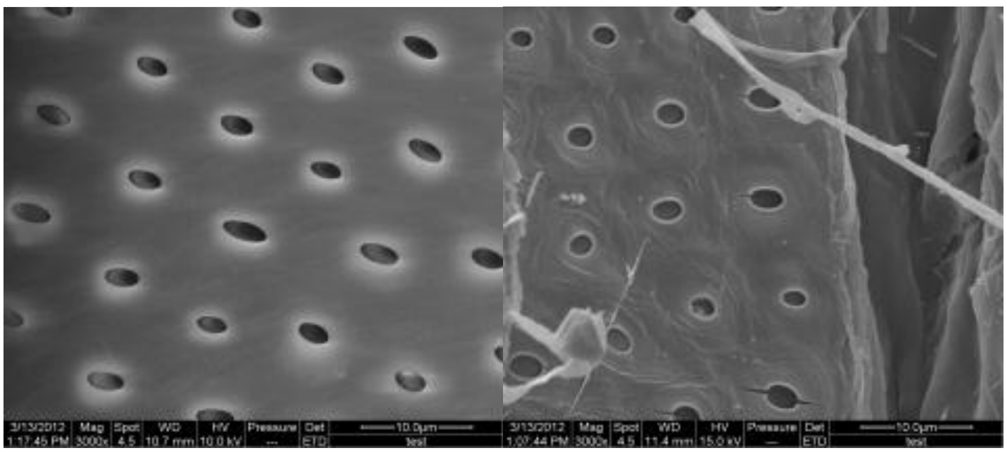

Fig. 2. Scanning electron microscopic images with magnification 10 µm of tangential section of control wood block before (left) and after (right) being exposed to fungus

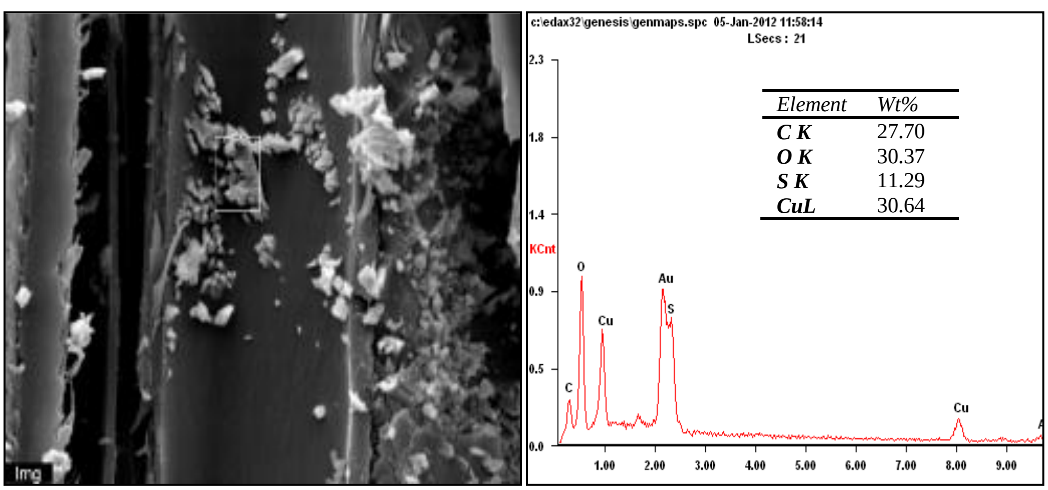

Fig. 3. SEM images with magnification 20 µm (left) and corresponding spectrum (right) of tangential section of unleached wood blocks treated with copper alone

Microscopic Observation and SEM-EDX Analysis

To confirm the effectiveness of copper fixation by the rosin sizing agent, SEM observation and energy-dispersive X-ray spectroscopy analysis (EDX) were used to identify the presence of copper in the copper-rosin treated and leached wood samples. Figure 2 shows the SEM images of the control wood sample before and after the fungal exposure. It can be clearly seen that the surface of wood cell wall of the control sample before the fungal exposure was extremely smooth (Fig. 2 left). After the fungal exposure, wood cell walls were completely destroyed by the fungi (Fig. 2 right). When the wood blocks treated with copper sulfate were observed, various crystal particles were found in the cell lumens (Fig. 3 left). The spot analysis using SEM-EDX proved that these particles contained Cu and S originating from copper sulfate (Fig. 3 right).

In the microscopic observation of the wood blocks treated with copper-rosin formulations, various spherical agglomerates were easily detected in the cell lumen (Fig. 4a and b left). The spectrum obtained from the spot analysis confirmed that these agglomerates contained the element Cu (Fig. 4a and b right). Unlike the crystals in Fig. 3, these agglomerates were tightly adhered to the wood cell wall. They had a lower Cu content and much higher C content in comparison to that observed in the crystal particles.

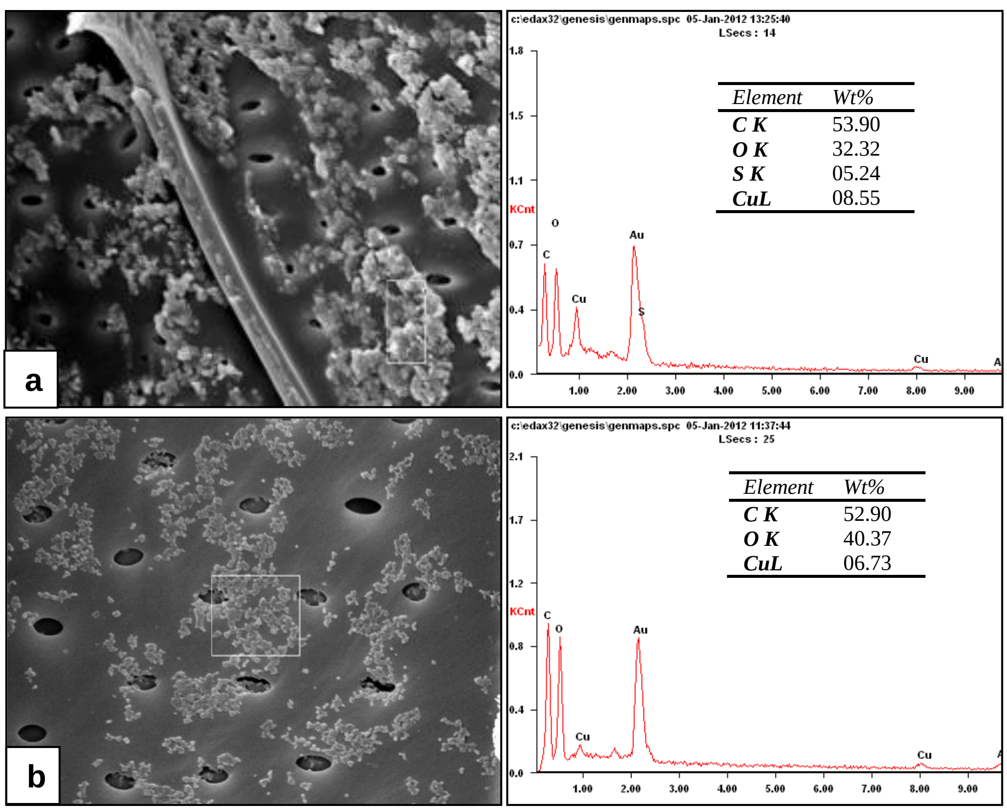

Fig. 4. SEM images (left side) and corresponding spectrum (right side) of tangential section of wood blocks treated with 2% Rosin + 3% $CuSO_4$: (a) unleached with magnification 20 μm and (b) leached with magnification 10 μm

This signifies that rosin interacted with copper and formed an adhesive film to cover the copper crystals. Therefore, Cu was fixed into the wood blocks. The SEM-EDX analysis results suggested that the presence of the preservative complexes containing Cu contributed to the good decay resistance of the leached wood blocks treated with the mixture of rosin size and copper sulfate.

CONCLUSIONS

1. This study evaluated the effect of rosin size on copper fixation and decay resistance of wood treated with copper sulfate and rosin sizing agent, separately or in combination, against white rot fungi *Trametes versicolor* and brown rot fungi *Gloeophyllum trabeum.* The samples impregnated with copper sulfate and the rosin sizing agent were more effective against fungal wood decay than those impregnated with only copper after leaching. Most of the leached wood samples treated with copper-rosin formulations showed less than approximately 3% weight loss. The rosin size agents themselves also showed poor performance against wood decay fungi.
2. The result of AAS analysis showed that rosin size had a certain effect on fixation of copper. The amount of copper ions released from the samples treated with the copper-rosin solutions was half those from the samples treated with copper alone.
3. The SEM observation and EDX analysis of the wood blocks treated with copper-rosin formulations confirmed that the preservative complexes containing Cu existed in the cell lumens of leached and decayed wood blocks.
4. This study may help in developing a new approach for using rosin size to reduce the hazard of the copper preservative leaching into the environment and lead to wood treated with water-borne copper preservatives being more widely used.

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