Fixation of a Water-borne Copper Preservative in Wood by a Rosin Sizing Agent

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Abstract

Samples of poplar wood (*Populus ussuriensis*) were treated with combinations of 3% $CuSO_4$ solution and 1.0%, 2.0%, or 4.0% rosin sizing agent. The fixation effect of copper preservative in wood and the efficacy of the preservatives against fungal decay was studied. The results showed that the treatment with only rosin sizing agent also had slight decay resistance. However, wood samples after being treated with the mixture of rosin sizing agent and $CuSO_4$ had good decay resistance. The average weight losses of the leached wood blocks samples degraded by both fungi *Trametes versicolor* and *Gloeophyllum trabeum* were less than 3%, were even lower than the non-leached samples. After leaching, the copper content in the leachates was analyzed by atomic absorption spectroscopy (AAS). Leaching copper from the samples treated with the copper-rosin solutions was only a half of those from the samples treated with copper alone. SEM-EDX analysis confirmed that the copper element was still in the cell lumens of leached wood blocks. This proved that the rosin sizing agent is very helpful to fix the copper preservative in wood. Therefore, the rosin sizing agent can reduce the hazard of the copper preservative leaching to the environment and help the wood treated with water-borne copper preservatives being used widely.

Keywords： rosin sizing agent, water-borne copper preservative, wood preservation, leaching resistant.

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Introduction

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 (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 was usually 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, CCA was completely banned in the European Union and limited to nonresidential uses in the United States (Townsend and Solo-Gabriele 2006).

Recently several methods have been researched to decrease copper leaching from wood, such as combined impregnation (Treu *et al.* 2011), incorporating additives into the preservative formulations (MitsuhashiGonzalez 2007), and combining copper with other co-biocides (Chen 2011; Humar et al. 2007). Some natural resources, such as enzymatic-hydrolyzed okara, soy protein products have been used to enhance the fixation of antifungal salts in wood structures (Ahn et al. 2010; Yang et al. 2006). Rosin, which comes from softwood, is abundant, natural, and renewable. It has a good hydrophobic and wood affinity. 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). In another study, non-solvent rosin-copper formulations with double impregnation have been proposed (Roussel *et al.* 2000) and treated wood blocks have shown good performance when leached. In addition, earlier investigations showed that a rosin sizing agent can improve the moisture absorbing ability of wood and also help improve wood decay resistance (Li et al. 2011; Li et al. 2009). Therefore, the aim of this research work was 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.

Materials And Methods

Preparation Sample and Treating Solutions

Wood specimens measuring 20 x 20 x 20 mm were prepared from air-dried sapwood of poplar trees (*Populus ussuriensis* Komo). Feeder strips (22 x 22 x 3 mm (longitudinal direction)) were also prepared from poplar sapwood.

The analytical copper sulfate ($CuSO_4$: Cu) was used as preservative salts to protect wood against fungal decay at one concentration of 3%. The anion rosin scattered 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%). 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.

Treating and Leaching Procedures

The wood blocks were first vacuum-treated for 30 minutes under a vacuum of 0.01 MPa followed by injection of the preservative mixture and then brought back to atmospheric pressure. After the blocks were completely saturated, they were removed from the solution and immediately weighed to ascertain the retention of each block. Then the treated samples were air-dried for 48 hours, oven-dried at 103 °C overnight, and reweighed to determine actual retention of each sample.

Leaching test was determined according to the American Wood Preservers' Association E11-07. The treated blocks were immersed in beakers of distilled water over which a vacuum was applied for 30 min. After the vacuum was released, the wood blocks were kept in the distilled water. After 6, 24, and 48 h and thereafter at 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 kept to measure the contents of copper leached from the treated wood blocks by using an atomic absorption spectroscopy (AAS) analyzer.

Decay Test

Decay test was evaluated in accordance with 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 mycelium of the test fungi, 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 bottles, brushed free of mycelium, dried at 103 °C overnight, and weighted to determine weight loss.

Microscopic Observation by SEM-EDX

After the decay test, 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 SEM.

Results And Discussion

Retention Results

Retention levels and percent actual 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, 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.

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

Solution and Concentrations	Theory Retention (kg/m^3)	Actual Retention (kg/m^3)	Treatability[a] (%)
1.0% R + 3.0% Cu	33.95 (0.93)[b]	33.48 (1.66)	98.38 (2.32)
2.0% R + 3.0% Cu	41.61 (1.69)	39.30 (2.07)	94.41 (2.17)
4.0% R + 3.0% Cu	58.32 (1.68)	52.29 (1.97)	89.66 (2.52)
3.0% Cu	26.06 (1.26)	25.05 (2.14)	96.01 (4.49)
1.0% R	7.9 (0.32)	7.75 (0.52)	98.22 (6.34)
2.0% R	15.83 (0.94)	15.32 (1.32)	96.91 (7.34)
4.0% R	31.72 (0.39)	27.06 (1.34)	85.33 (6.23)

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

There were slight differences in the treatability of the three rosin formulations. The actual percent retention of preservative solution-containing rosin decreased from 98.22 to 85.33% with the increase in concentration of rosin from 1.0 to 4.0% in the impregnation solution. An explanation for this would be that when the concentration of rosin increases, the emulsion viscosity increases, which might be partially responsible for decreasing the actual retention of preservatives. However, this decrease was not significant and the highest retention was obtained with 1% rosin size and 3% added copper sulfate.

Copper Leaching

The analyzed results of copper ions released from blocks treated with the copper-rosin solutions and those treated with the copper sulfate alone taken at different time intervals is 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 (Fig. 1). A large amount of copper ions was 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. However, the total amount of copper ions release from the samples treated with the copper-rosin solutions was 2 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 decreases with the increase of rosin concentration in the impregnation mixture. However, this difference was not significant and the results suggest that the rosin sizing agent in three concentrations had also a certain effect on the fixation of copper.

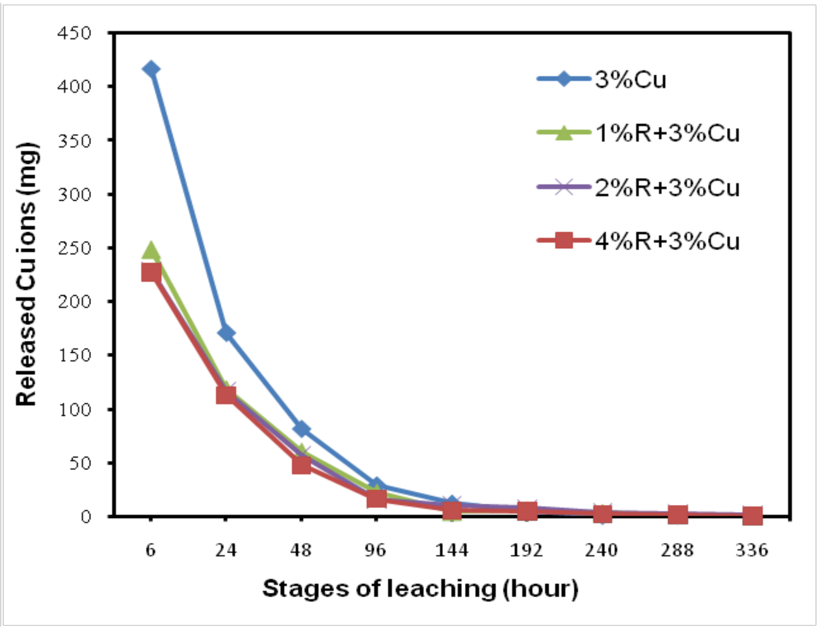

Figure 1. *Copper ions released from treated wood specimens at different time intervals.*

Decay Resistance

The results from the decay test are shown in Fig. 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 had approximately 4% or less weight loss for both test fungi. However, a severe weight loss (approximately 40%) was found for the leached wood samples treated with only copper.

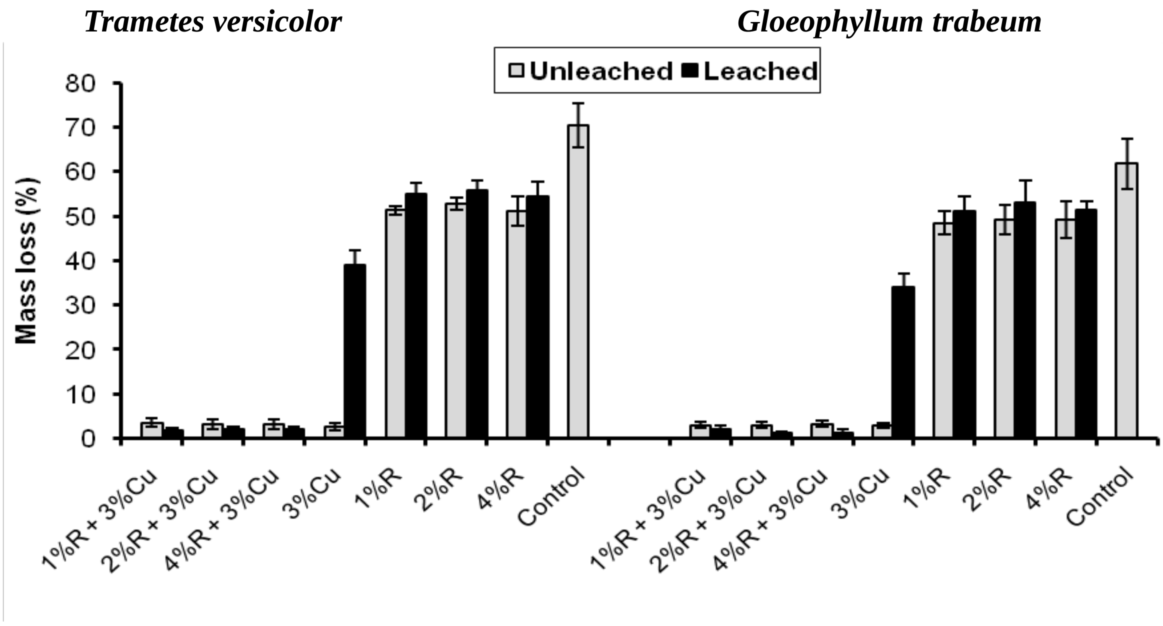

Figure 2. *Weight loss (%) of samples exposed to T. versicolor and G. trabeum attack.*

For the samples treated with only rosin sizing agents and leached had weight losses in the range of 48-55%, which was much lower than those of the untreated control 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). However, the samples treated with copper-rosin formulations showed good decay resistance against both *Trametes versicolor* and *Gloeophyllum trabeum*. After 12 weeks, the average weight loss of the samples degraded by fungi was approximately 4%. The leached wood blocks treated with copper-rosin formulations showed less than 3% weight loss and were not entirely covered by mycelium of both test fungi. Therefore, the use of rosin size as fixed agents may reduce environmental impact of wood treated with copper-based preservatives.

Microscopic Observation and Analysis

Figure 3 shows the SEM images of the control wood sample before and after the fungal exposure. It can be clearly seen that surface of wood cell wall of the control sample before the fungal exposure was extremely smooth (Fig. 3 left). After the fungal exposure, wood cell walls have been completely destroyed by the fungi (Fig. 3 right). When the wood blocks treated with copper sulfate alone and combination with rosin were observed, various crystal particles as well as spherical agglomerates were found in the cell lumens (Fig. 4).

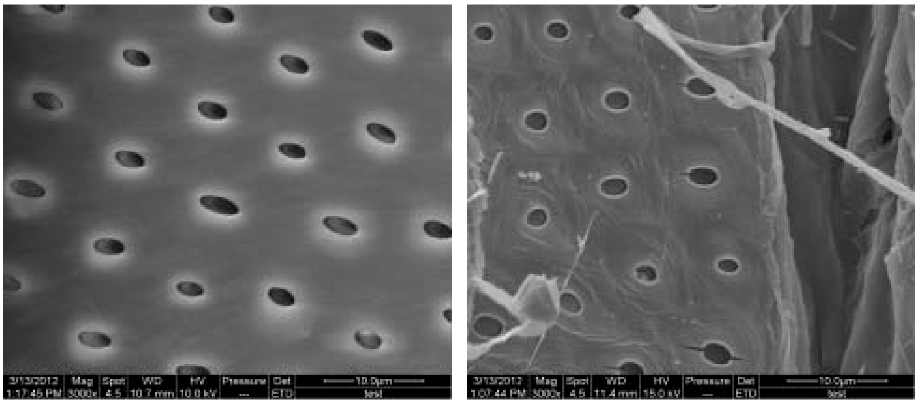

Figure 3. *Scanning electron microscopic images of control wood block before (left) and after (right) exposed to fungus.*

In the microscopic observation of the wood blocks treated with copper-rosin after leaching and decay, various spherical agglomerates were easily detected in the cell lumen (Fig. 5a,b). The spectrum obtained from the spot analysis confirmed that these agglomerates contained the element Cu (Fig. 5c,d). This signifies 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.

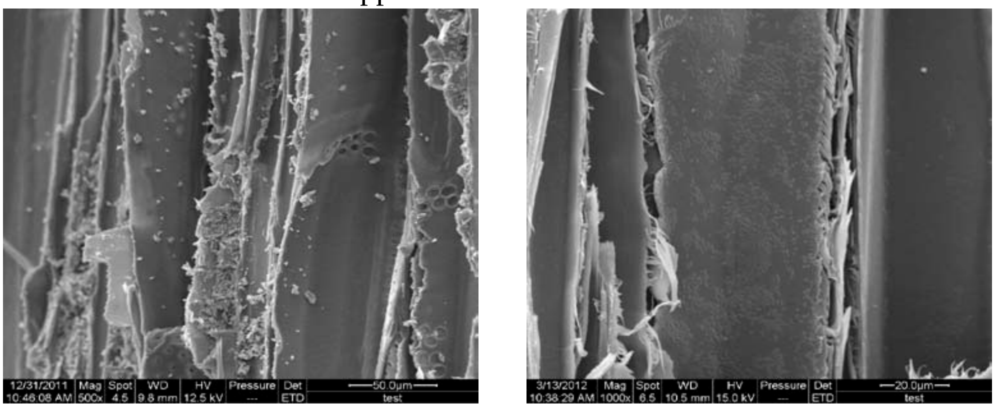

Figure 4. *SEM images of unleached wood blocks treated with copper alone (left) and with copper-rosin (right).*

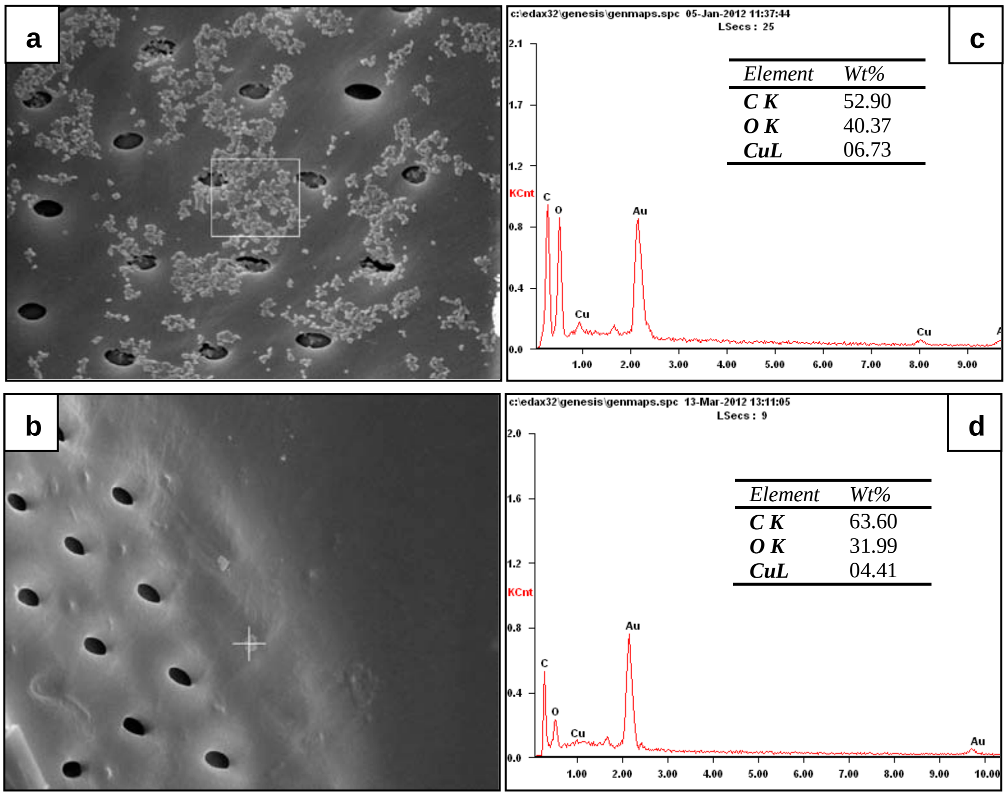

Figure 5. *SEM images (left side) and corresponding spectrum (right side) of wood blocks treated with copper-rosin: (a,c) after leached and (b,d) after leached and decayed.*

Conclusions

This study determined 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 results showed that, poplar wood after being treated with copper-rosin solutions were more effective against fungal wood decay than those impregnated with only copper after leaching. The average weight losses of the samples degraded by fungi were less than approximately 3%. The rosin size agents themselves also showed poor performance against wood decay fungi. The result of AAS analysis showed the amount of copper ions released from the samples treated with the copper-rosin solutions were 2 times less than those from the samples treated with copper alone. The SEM-EDX analysis of the wood blocks treated with copper-rosin confirmed that the element Cu existed in the cell lumens of leached and decayed wood blocks.

Acknowledgements

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Tables Cited

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