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Analyses of Impregnation Quality and Mechanical Properties of Radiata Pine Wood Treated with Copper Nanoparticle- and Micronized-Copper-Based Wood Preservatives

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Abstract: In this work, the impregnation quality and mechanical properties of *Pinus radiata* D.Don treated with different copper nanoparticles (CuNP) solutions (named K1 and K2) and a commercial preservative (M) were studied. The impregnation quality of radiata pine wood was analyzed by two indicators, penetration and retention. The micro-distribution of preservative in the treated wood was qualitatively evaluated by SEM-EDS, both in the samples containing CuNP and in those treated with the commercial preservative. In addition, some mechanical properties were studied in the preserved wood including MOE, MOR and hardness. The results indicated values by ED XRF retention of 0.96 kg/m^3 and 0.86 kg/m^3 for K1 and K2, respectively, and 1.01 kg/m^3 for M wood impregnated. In the penetration determined by colorimetric test, the wood samples impregnated (with K1, K2 and M) showed 100% penetration. The distribution of CuNP and micronized copper within the wood structure was confirmed by SEM EDS mapping. In mechanical properties, a reduction in MOE was reflected in all wood treated. The control samples were far superior to the K1 and M treated samples and slightly superior to the K2 samples, with no statistically significant differences. On the other hand, samples impregnated with K1 and K2 showed the highest values in hardness parallel and perpendicular to the grain, revealing that these preservative solutions tend to increase hardness. Overall, when it comes to the samples impregnated with micronized copper (M), the mechanical properties were considerably lower compared to the CuNP treated and control wood. Therefore, the CuNP-based preservative did not strongly affect the mechanical properties of the preserved wood.

Keywords: wood preservation; copper nanoparticles; retention; mechanical properties

Citation: Aguayo, M.G.; Erazo, O.; Montero, C.; Reyes, L.; Gacitúa, W.; Gómez, L.; Torres, H. Analyses of Impregnation Quality and Mechanical Properties of Radiata Pine Wood Treated with Copper Nanoparticle- and Micronized-Copper-Based Wood Preservatives. *Forests* **2022**, *13*, 1636. https://doi.org/10.3390/f13101636

Academic Editors: Jorge Santos and Danilo Escobar-Avello

Received: 25 August 2022
Accepted: 22 September 2022
Published: 6 October 2022

1. Introduction

Wood occupies a prominent place as a building material due to its attractive properties such as mechanical strength and low thermal expansion compared to other building materials [1]. Most wood species commonly used in construction deteriorate if exposed to conditions that support the growth of wood degrading organisms [2]. This deterioration drastically decreases the strength properties of wood and creates a challenge in controlling and analyzing various factors, including the physical-chemical factors that have a potential impact on the useful life of wood [3].

One of the most common treatments applied in wood preservation is pressure treatment, which uses a combination of vacuum and pressure to force penetration of chemical preservatives into the cellular structure of the wood [4]. In wood preservative impregnation, there are four processes in which pressure is used, full cell, modified full cell, empty cell and double-vacuum process [5–7]. Prior to treatment, the wood must be dried to the ideal

moisture content for CCA impregnation. The removal of water from the lumen and inter- and intracellular spaces leaves voids to facilitate chemical penetration. However, it should be noted that the treatability of wood is greatly related to its porous structure. Moreover, it can be influenced by other parameters such as wood moisture content, drying technique, preservative formulation and others [8].

The permanence of a chemical preservative in wood is the single most important factor that determines the effectiveness of the preservative system. Various wood preservatives have been used in pressure-treated wood to extend the shelf life and improve the performance of wood products. These preservatives mainly include metal compounds that can be solubilized in water and are effective against wood-destroying organisms [7]. The most used wood preservatives are chromated copper arsenate (CCA), ammoniacal copper zinc arsenate (ACZA), alkaline copper quat (ACQ) and copper azole [9]. In recent years, the industry and research on wood protection have focused on the development of preservatives based on nano- and micronized particles [10].

The potential of wood as a building material is widely known. However, wood's performance is limited by external factors decreasing its properties. Therefore, wood species classified as non-durable must be preserved according to standard requirements for use in construction. Winandy [11] extensively reviewed the effects of treatment with conventional preservative chemicals (mainly soluble copper-based) on various mechanical properties of wood. They noted that each mechanical property was differently affected by the preservative treatment. In one of the conclusions to this analysis, they also indicated that the MOE in impregnated wood is not usually affected. Similar antecedents were found by Sukla et al. [12], who determined the MOE in rubberwood impregnated with micronized copper azole (MCA) and chromated copper arsenate (CCA). The results showed no statistically significant difference in the MOE of rubberwood samples treated with different copper concentrations. However, when compared to controls, there was a significant variation in the MOR of specimens impregnated with 0.5%–2% MCA, but no differences were found in the MOR of wood treated with 1%–2% MCA and 2 h of impregnation. Barnes et al. [13] also reported similar results on southern pine treated with micronized preservative systems; however, bending properties of certain hardwoods were found to be reduced due to preservative impregnation suggesting that treatments may have some negative impact on strength properties.

It is well known that nanotechnology has great potential for wood preservatives. The use of nanometer-sized metallic preservatives allows for a deeper and more homogeneous penetration of the particles into the wood. The microdistribution of preservatives containing nanoparticles in wood is different from those of common water-borne preservatives because most of these particles are too large to penetrate the microporosity of the cell wall [14]. The use of nanoparticles in wood preservation has been evaluated in different research works, mainly focusing on the fungal degradation, leaching of bioactive compounds [2,7,15–17] and the performance of wood treated with metal nanoparticles in termite bioassays [18,19]. However, there is scarce information about the mechanical properties of nanoparticles-treated wood, being that the physic-mechanical properties of wood provide important information for its classification, as well as quality indicators for its use in construction [20]. The present study aimed to analyze the impregnation quality and mechanical properties of radiata pine wood treated with copper micronized and copper-nanoparticle-based solutions. Additionally, scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) analyses were used to identify the presence of solid copper particles in the microstructure of radiata pine wood.

2. Materials and Methods

2.1. Raw Materials

Commercial *Pinus radiata* D. Don wood was provided by Promaest Ltd.a. sawmill (Los Angeles, Chile). From the wood bundles normally marketed by the company (25 mm × 100 mm × 3050 mm and 50 mm × 75 mm × 3050 mm), about 50 sapwood pieces with

at least three growth rings in cross section were taken. Subsequently, these pieces were dimensioned according to the requirements of each test; for static bending, retention and penetration tests, 110 samples of 25 mm × 25 mm × 410 mm were used, and for density, 90 samples of 25 mm × 25 mm × 100 mm were used. For hardness, 80 samples of 50 mm × 50 mm × 150 mm were used. The samples were free of cracks, knots, stains or any other defects. Density of radiata pine wood was determined according to ASTM D 2395 [21]. The pieces had an average density of 415 kg/m^3, from 30 samples measured. The micronized copper, a commercial preservative used for radiata pine wood, was provided by the same company, with copper particle size ranging from 50 nm to 1 µm. Copper nanoparticle (CuNP) solutions were provided by NanoProcess SpA company (Antofagasta, Chile). Some of the CuNP's characteristics in solution used in this study were reported in a previous work, such as the average NP size of 24 nm, polydispersity index of 0.375 and Z-potential of −15.0 mV [2].

2.2. Wood Impregnation

Radiata pine wood was impregnated by the Bethell process in an impregnation cylinder of 48 L capacity. Three preservative solutions were used, two CuNP-based solutions and a commercial preservative, micronized copper. The characteristics of each preservative solution used in this research are shown in Table 1. A set of 70 specimens (20 for static bending, 20 for hardness, 10 for retention and penetration and 20 for density) were used in the impregnation for each preservative solution. The impregnation process parameters were: initial vacuum at −20 mmHg for 30 min followed by flooding with the preservative solution. Then, an impregnation pressure of 6 bar was applied to the wood samples for 90 min. Once the impregnation was completed and the remaining solution was drained, a vacuum at −20 mmHg was applied for 15 min to remove the excess solution. The impregnated samples were dried and stored at a temperature between 20 and 25 °C for 72 h.

Table 1. Preservative solution concentrations used in radiata pine wood impregnation.

Preservative Solutions	Designation	Solution Concentration (%)
CuNP-based + A [1]	K1	0.31
CuNP-based + B [1]	K2	0.35
Micronized copper	M	0.56

[1] A and B, different formulations based on stabilizing and dispersing additives.

2.3. Retention and Penetration of Impregnated Wood

The copper retention of impregnated wood samples was determined by Energy Dispersive X-ray Fluorescence Analysis (ED XRF) according to the AWPA A9-18 [22] procedure. To analyze the CuNP impregnated samples, a calibration curve for ED XRF was prepared with five calibration points by using a copper standard solution (Centipur®, Merck, Darmstadt, Germany), which was diluted in water and manually mixed with the radiata pine milled wood as a solid matrix. To analyze the micronized-copper-impregnated samples, the calibration curve of this product was used, prepared under the AWPA certified standards, available at the Preserved Wood Quality Control Laboratory of the Universidad del Bío-Bío.

Each impregnated sample was chipped, milled and sieved to 30 mesh. Then, each sample was dried in a drying chamber to a constant weight at 105 °C and cooled in a desiccator. Each sample was placed in a 32 mm XRF sample holder with Mylar® film, pressed to 250 in-lbs. The samples were read on an EDXRF spectrometer (Rigaku Nex QC, Austin, TX, USA). The retention value for each treatment was obtained as the 10 samples read in ED XRF average.

The preservative penetration into the wood after the impregnation process was evaluated according to the protocol established by AWPA A69-18 [23]. This protocol consists of performing a colorimetric staining test with a Chrome Azurol S solution, which is applied by spraying the solution on the internal cross-section (assay zone) of the impregnated

sample. To identify the assay zone, it was verified in AWPA T1-18 [24] according to the thickness of impregnated sample.

2.4. Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on wood samples impregnated with CuNP and M solutions. For each impregnated sample, specimens of 5 mm per side were prepared and mounted on stubs to apply a conductive coating using a metallizer (sputter-coated). The coating was performed with gold for 30 s. Images were taken using a JEOL-JSM 6380LV scanning electron microscope (Tokyo, Japan) coupled to X-Max EDS detector system (Oxford Instruments, Oxford, UK). Image mapping was obtained with AztecOne software (4.2 SP1, Oxford Instruments Nanotechnology Tools Lmt.). Each treated wood sample (K1, K2 and M) was observed in triplicate.

2.5. Mechanical Properties

Static bending tests were performed in a Zwick/Roell Z020 Universal Testing Machine (ZwickRoell GmbH & Co. KG, Ulm, Germany) with a maximum load cell capacity of 20 kN, equipped with an extensometer. The samples were previously conditioned in a climatic chamber (Memmert, Schwabach, Germany) at a temperature of 21 °C and a relative humidity of 65%, until an equilibrium moisture content of 12% was reached. The tests were performed in accordance to ASTM D143 [25], and the secondary method was considered to the specimen dimensions. Twenty specimens of 25 × 25 × 410 mm dimensions for each impregnation process (K1, K2 and M) and control samples were tested on the longitudinal tangential face nearest to the pith at a cross-head speed of 1.3 mm/min. The linear portion of the stress–strain curve was used to determine the modulus of elasticity (MOE) and the modulus of rupture (MOR), calculated according to Equations (1) and (2), respectively:

$$MOE = \frac{P\,L^3}{4\,D\,b\,h^3} \quad (1)$$

$$MOR = \frac{3\,P_{max}\,L}{2\,b\,h^2} \quad (2)$$

where P is the load at the limit of proportionality (N), P_{max} is the maximum load (N), L is the distance between the beam support (mm), D is the deflection at the proportionality limit (mm), b is beam width (mm) and h is beam thickness (mm).

Hardness tests were performed according to the ASTM D143 [25]. Twenty 50 × 50 × 150 mm specimens were used for each impregnation process (K1, K2 and M) as well as control samples. An Instron Universal Testing Machine (Model 4468, Instron Corp., Canton, OH, USA) with cell load of 50 kN, equipped with an 11.3 mm diameter steel ball for indentation. Each test was performed at 6 mm/min speed and indented at two different positions on the radial and tangential surfaces. The average values of the maximum load were used to determine the hardness parallel and hardness perpendicular to the grain.

2.6. Data Analyses

The mechanical test data were analyzed using the statistical package software SPSS version 21 (IBM Corp. Armonk, NY, USA). The significant differences for all treatments were statistically evaluated by one-way ANOVA ($p < 0.05$), and the difference among the mean values of the treatments was determined using Tukey's multiple range test.

3. Results and Discussion

3.1. Quality of Impregnated Radiata Pine Wood

3.1.1. Impregnation Process—Retention Performance

The impregnation efficiency is determined by two indicators, one qualitative and the other quantitative, namely, penetration and retention, respectively [26,27]. After radiata

pine wood impregnations, the retention by ED XRF values for the different preservative solutions were: K1, retention of 0.96 kg/m^3 and 421 kg/m^3 density; for K2, retention of 0.86 kg/m^3 and 415 kg/m^3 density; and for M, retention of 1.01 kg/m^3 with 418 kg/m^3 density, as shown in Figure 1. The required retention of each preservative product in the impregnated wood depends on the use of the wood and its risk of biodeterioration once put into service. According to AWPA U1-18 [28] and Chilean standard NCh 819 [29], the minimum required retention of micronized copper in radiata pine wood is 1.00 kg/m^3 (for risk levels 1, 2 and 3). For radiata pine wood impregnated with CuNP, there is no specific standard indicating the minimum required retention of this product. However, it should be noted that the risk levels are associated with use of wood (outdoor or indoor use) and the fungicidal and insecticidal effectiveness of preserved wood. Studies of fungal resistance of wood impregnated with CuNP have been reported, where the CuNP effectiveness against certain fungi has been confirmed [2,7,14,15,19]. Recently, Aguayo et al. [2] reported that radiata pine wood impregnated with CuNP is effective against brown rot fungi. For ED XRF retention values between 0.64 kg/m^3 and 1.68 kg/m^3, the mass loss in the samples inoculated with *Gloeophyllum trabeum* and *Rhodonia placenta* was less than 5%.

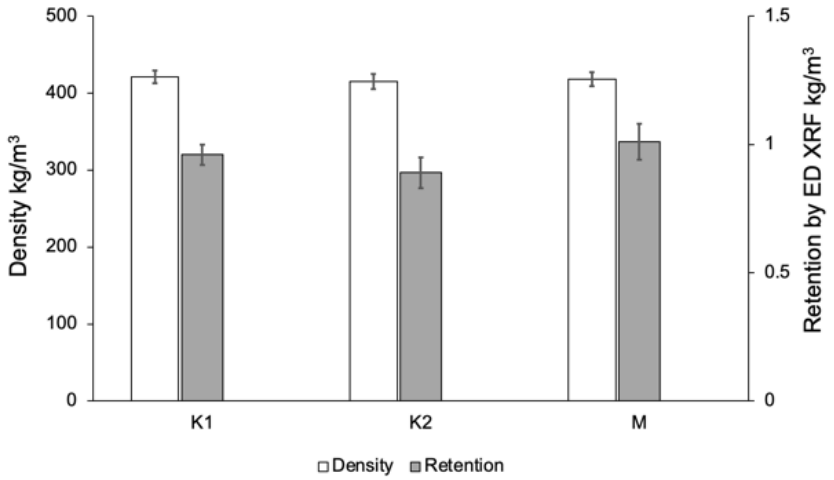


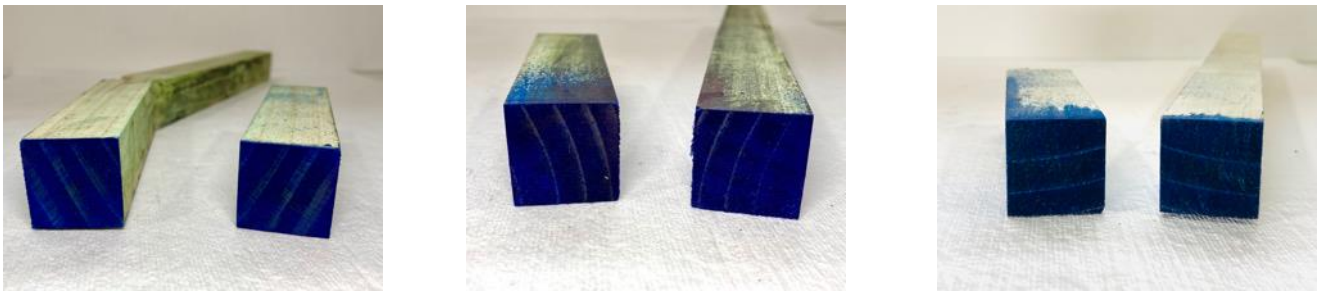
Figure 1. Density (primary axis) and Retention by ED XRF (secondary axis) of radiata pine wood impregnated with K1, K2 and M. The maximum standard error for density was 10 kg/m^3 and 0.07 kg/m^3 for ED XRF retention.

Several investigations have been reported on wood impregnated with copper nanoparticles. Bak and Nemeth [16] evaluated the effect of pine (*Pinus sylvestris*) and beech (*Fagus sylvatica*) wood treated with different nanoparticles, including CuNP. The authors reported that pine samples presented high chemical retention values compared to beech samples, where pine wood impregnated with CuNP at a concentration of 0.5% obtained a chemical retention of 2.85 kg/m^3. Pařil et al. [15] impregnated Scots pine sapwood with copper nanoparticles. They reported 2.08 kg/m^3 retention for samples impregnated with a 3 g/L CuNP solution (0.3% CuNP concentration). The retention was calculated based on the CuNP concentration. These values were higher than the retention values by ED XRF, since the value of chemical retention was calculated from the CuNP concentration solution and it was considered as the absorption value of the preservative solution in the wood block after impregnation [30].

3.1.2. Penetrability Characteristics of the Used Preservatives

Sampling after impregnation process is a standard practice for evaluation of preservative retention levels in preservative-treated wood [31]. The depth of penetration of some preservatives can be measured with the help of the color change of the treated wood, where the chemical reagent reacts with the active components of the preservative in the impregnated wood [8,32]. A Chrome Azurol S solution, a color indicator for copper, was applied

to the impregnated samples, K1, K2 and M, in the 2.5 cm × 2.5 cm cross-section, indicating an intense blue coloration in the three samples (Figure 2). AWPA T1-18 [24] requires that for radiata pine lumber <50 mm thick, the assay zone for determining penetration be measured on a cross-section cut at a point where the piece is approximately 15 mm (0.6 in) thick. Therefore, our samples achieved 100% penetration.



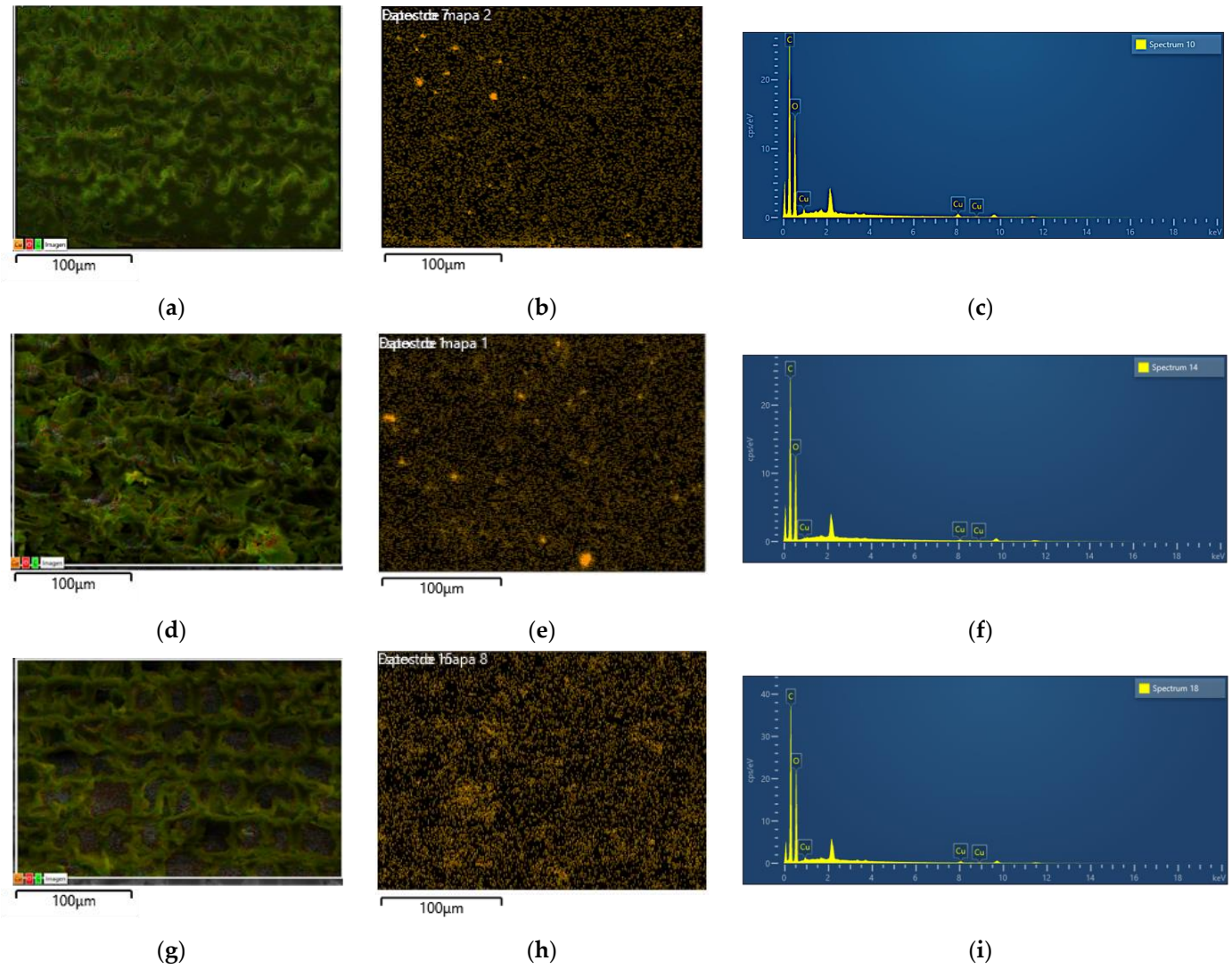
(**a**) (**b**) (**c**)

Figure 2. Copper penetration in treated wood. Blue color indicates copper in (**a**) K1 CuNP-treated wood, (**b**) K2 CuNP-treated wood and (**c**) micronized-copper-treated wood.

Tripathi and Kumar Poonia [4] determined the penetration of preservatives, including CCA, in Melia composita samples of size 3.8 cm × 3.8 cm × 30.5 cm, which were transversely cut in the center of the sample to expose a fresh cross-section with Chrome Azurol S. The penetration of CCA into sapwood was 100%, while in heartwood it did not exceed 45%. Lebow et al. [31] studied copper penetration using a Chrome Azurol S solution in a Southern pine species group. The penetration was generally good in copper azole and micronized-copper-treated wood, except in those areas where the impermeable heartwood or knots were close to the surface. The Chrome Azurol S test on preserved wood is a quick technique to be applied in the wood preserving industry, where it is necessary to immediately identify the right dispersion of the preservative in the wood.

3.2. Copper Particle Distribution in Treated Wood by SEM-EDS

The presence of copper in the cross-section within K1, K2 and M treated wood was confirmed by SEM-EDS mapping and X-ray spectroscopy (Figure 3). SEM-EDS mapping for K1 and K2 showed a uniform distribution of copper in the cross-section of the treated wood (Figure 3a,e). In the case of K1, small concentrations of copper were observed, identified by a strong orange color. Similarly, M samples presented a uniform dispersion in the cross-section of the impregnated wood, and in this case, there was a slightly higher copper concentration in the cell lumina (Figure 3g,h). Wang and Qi [33] indicated that copper-treated wood can retain copper in the cellular components of the wood after the fixing and drying stage. They also indicated that the type and distribution of copper in wood are dominated by several factors, such as particle size, transport pathways and the availability of deposition/reaction sites where particles accumulate. Therefore, the proper anatomical structure of radiata pine wood allows for a better distribution of the preservative particles in wood, as a result of fiber and lumen size (>10 µm) and pit aperture close to 5 µm [17]. This allows for the good performance of CuNP, which, in our case, was 24 nm in size in the wood impregnation process. As mentioned in methodology, sapwood pieces with at least three growth rings were used. The sapwood is more permeable than heartwood. Preservatives can flow through axial and radial resin canals and ray parenchyma cells in both fusiform and uniseriate rays [34]. On the other hand, even when the drying process causes pit aspiration, pits in latewood tend to be less aspirated than earlywood because of its membrane structure [17]. Moreover, during the pressure treatment of wood with preservatives, pit membranes are often ruptured and allow preservatives to pass through the structure [14,35].



(**a**) (**b**) (**c**)

(**d**) (**e**) (**f**)

(**g**) (**h**) (**i**)

Figure 3. SEM-EDS map for copper of (**a**,**b**) K1-treated wood, (**d**,**e**) K2-treated wood and (**g**,**h**) micronized-copper-treated wood. EDS spectrum of K1 (**c**), K2 (**f**) and M (**i**).

The distribution of CuNP found in this work agrees with that reported by Matsunaga et al. [14] on the microdistribution of copper carbonate and iron oxide nanoparticles in treated Southern pine wood, as well as the work reported by Wang and Qi [33], who analyzed the distribution of micronized copper azoles in impregnated yellow pine wood.

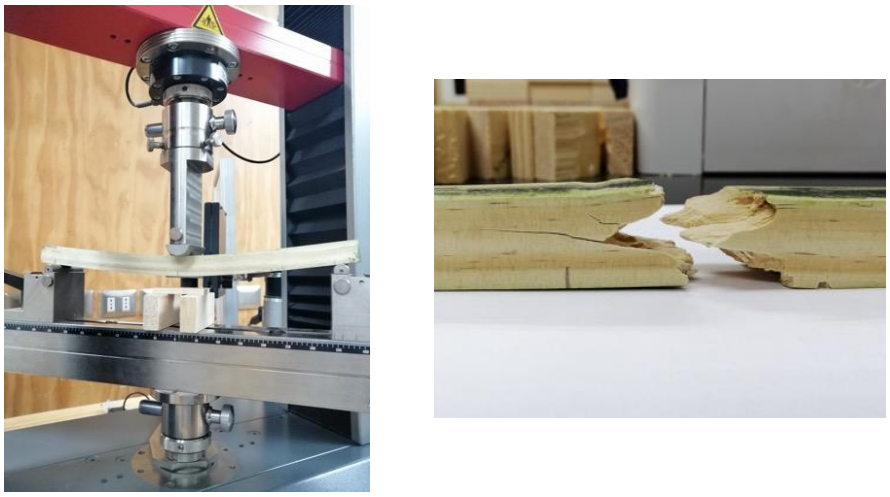
The EDS analysis spectra (Figure 3c,f,i) show the presence of Cu. Moreover, elements such as oxygen (O) and carbon (C) were detected, which were related to the wood composition itself. In addition, a gold signal was observed due to the metallization of the sample to aid in image conduction and observation.

3.3. Mechanical Properties Evaluation

3.3.1. Static Bending

The samples impregnated with the preservatives K1, K2 and M were subjected to static bending tests. Figure 4a shows an impregnated wood specimen being tested by the Zwick/Roell Z020 universal testing machine and Figure 4b the splintering tension type of failure, which caused the sample to split into two parts. This type of failure was observed in most specimens tested (control and impregnated specimens). The mean values of the modulus of rupture (MOR) and the modulus of elasticity (MOE) in static bending for the control and impregnated specimens are shown in Table 1. The results of the variance analysis determined that there were significant differences in all treatments,

which presented a p-value < 0.001. Specifically, the control samples presented a higher MOE (10.29 GPa), followed by the samples treated with K2 (9.45 GPa), while the samples impregnated with M presented the lowest MOE (7.72 GPa), which represented a decrease of 24.94% with respect to the control values. This reduction can be attributed to the high variability of the wood, as reflected in the high coefficient of variation (27.8%).



(**a**) (**b**)

Figure 4. Photographs of the static bending test: (**a**) load applied to an impregnated wood sample by the Zwick/Roell Z020 universal testing machine and (**b**) failure generated in the specimen after the test was completed.

On the other hand, Tukey's HSD test did not detect significant differences between the K2 treatment (9.44 GPa) and control samples, indicating that there was no effect of the preservative on the wood stiffness. Similarly, Barnes et al. [13], in a study carried out with CCA salts and copper xyligen, found a decline (<9%) in the MOE in the treated samples. However, they reported no significant differences between the treated and control samples. Likewise, Yildiz et al. [36] obtained slightly higher MOEs in the untreated specimens than in samples treated with ACQ, CCA and Tanalith, but this increase in MOE was not statistically significant. This behavior was also reported by Shukla et al. [12] in samples treated with copper azoles and CCA, which presented moduli of elasticity slightly lower than those found in the control samples.

Concerning the modulus of rupture, the treatments presented significant differences (p-value < 0.001). The pieces treated with K2 had a MOR of 80.6 MPa, which is slightly higher than that reported in the control specimens (75.7 MPa). Like MOE behavior, Tukey's test revealed that MOR had no significant differences between the K2-treated and control specimens. However, quite the opposite was found for the samples treated with M and K1: there were significant differences, which indicated a reduction of 37% and 19% with respect to K2. This drop in MOR was more noticeable in the pieces treated with M, which had the lowest MOR value. Therefore, there was an effect of the preservative on the mechanical properties, which can be attributed to the interaction of both the wood and preservative functional groups [12]. Additionally, the type of preservative and treatment may condition the mechanical performance of wood when it is subjected to an impregnation treatment. This has been observed in several investigations, in which, some researchers have reported no effect of the preservative on MOR [13,36], while others have shown the opposite [12].

3.3.2. Hardness

The results of the parallel and perpendicular to the grain hardness for the control and treated specimens are presented in Table 2. The perpendicular hardness resulted from the average of the hardness measured in both the radial and tangential anatomical directions,

which presented no differences between them. Variance analysis indicated significant differences between the perpendicular and parallel hardness (p-value < 0.001).

Table 2. Mechanical properties mean values and coefficient of variation of the analyzed studied samples.

	MOE (MPa)		MOR (MPa)		Perpendicular Hardness (kN)		Parallel Hardness (kN)	
Samples	**Mean**	**CoV * (%)**	**Mean**	**CoV *(%)**	**Mean**	**CoV * (%)**	**Mean**	**CoV * (%)**
Control	10289 ^{a} (1384)	13.5	75.7 ^{a} (7.9)	10.4	1.78 ^{a} (0.39)	22.0	3.12 ^{a} (0.60)	19.2
K1	8273 ^{b} (1507)	18.2	65.0 ^{b} (17.1)	26.3	2.08 ^{a} (0.58)	27.6	3.81 ^{b} (0.71)	18.6
K2	9447 ^{ab} (1794)	19.0	80.6 ^{a} (13.1)	16.2	2.09 ^{a} (0.39)	18.6	4.11 ^{b} (0.46)	11.2
M	7723 ^{bc} (2149)	27.8	50.7 ^{c} (8.0)	15.7	1.47 ^{b} (0.31)	21.3	2.62 ^{a} (0.43)	16.6
F-test	8.84		23.42		6.32		17.89	
p-value	<0.001 **		<0.001 **		<0.001 **		<0.001 **	

* CoV is the variation coefficient in percentage. Standard deviation in parenthesis. ** Significative at 5% of probability with F-test. Lowercase letters indicate significant differences between wood treated.

For the perpendicular hardness, Tukey's multiple range test showed that the control and K1 and K2 treated specimens did not differ statistically from each other; however, the highest hardness values were found for K1 (2.08 kN) and K2 (2.09 kN). These values indicated an increase of 14% in hardness compared to the control hardness value (1.47 kN). Likewise, the parallel hardness to the grain was higher in the K1- and K2-treated specimens. Although K2-treated pieces had a higher hardness value, there was no difference between them. This high value in K2 (4.01 kN) hardness increased by 36% with respect to the control specimens (3.12 kN). On the other hand, when observing the perpendicular and parallel hardness values, the pieces treated with M presented the lowest values, which reflect that there was an effect of the preservative on the hardness.

When compared to perpendicular hardness, it is evident that pieces had different outcomes, in fact, there was an increase between 43% and 49% higher than the perpendicular hardness. This behavior has also been found by other researchers [37–39]. The reason that the parallel direction hardness is higher is due to the longitudinal arrangement of the fibers in the load direction; that is, the load is supported by the bundle of fibers that make up the piece's structure. The opposite effect occurs when the fibers' axis direction moves away from the load direction. In this case, both the number of fibers and stiffness decrease [40]. Likewise, the cellulose microfibril angle has an influence on the wood hardness; therefore, hardness is highly dependent on the direction of the applied load. This may explain the variability in this property [40]. Otherwise, the increase in hardness for samples K1 and K2 may be due to the distribution of copper nanoparticles within the wood structure. This has been reported for the hardness of the fiber cell walls impregnated with copper nanoparticles and modified resin. Researchers found that the copper nanoparticles diffused easily into the intercellular spaces and the cell wall and the formation of a complex cross-linking in the cell wall [41]. This contrasts with water-borne solutions that use metal oxides, which undergo a hydrolytic reaction when reacting with hemicelluloses; therefore, they end up oxidizing the cell wall components and consequently reduce the properties of wood [42].

4. Conclusions

The impregnation quality and the mechanical properties of radiata pine wood treated with two preservative solutions based on copper nanoparticles (K1 and K2) and a commercial preservative, micronized copper (M), were analyzed. The effectiveness of the impregnation was determined by two indicators, penetration and retention. The required retention of each preservative in the impregnated wood depends on the use of the wood and its biodeterioration risk once put into service. Therefore, there are only standardized records for micronized copper (minimum required by the NCh 819 standard of 1 kg/m^3).

For wood impregnated with CuNP, there is no standard indicating the minimum retention required. For the penetration determined by colorimetric test, the three impregnated wood samples showed 100% preservative solution penetration. The distribution of copper nanoparticles and micronized copper within the wood structure was confirmed by SEM EDS. In the mechanical properties, a reduction in MOE was reflected for all wood treatments. The control samples were far superior to the samples treated with K1 and M and slightly superior to the K2 treatment, with no statistically significant differences. In the case of MOR, the samples treated with K2 showed a slight increase compared to the control. On the other hand, samples impregnated with K1 and K2 showed the highest values in hardness parallel and perpendicular to the grain, revealing that these preservative solutions tend to increase hardness. In general, when it comes to the preserved M samples, the mechanical properties were considerably lower for the copper nanoparticles-treated and control wood. Therefore, the copper-nanoparticle-based preservative solutions did not strongly affect the mechanical properties of the wood, making these preservative products an additional alternative for the preserved wood industry.

Author Contributions: Conceptualization, M.G.A. and L.R.; methodology, M.G.A., O.E. and C.M.; validation, O.E. and C.M.; formal analysis, M.G.A., O.E. and C.M.; investigation, M.G.A. and L.R.; resources, M.G.A., L.G. and H.T.; data curation, O.E. and C.M.; writing—original draft preparation, M.G.A., O.E. and C.M.; writing—review and editing, L.R., W.G., O.E. and C.M.; visualization, M.G.A., W.G., L.G. and H.T.; supervision, M.G.A., L.R. and W.G.; project administration, M.G.A. and L.R.; funding acquisition, M.G.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by CONICYT FONDEF IDeA I+D 2019, grant number ID19I10122.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: María Graciela Aguayo is grateful for the technical support of Jorge Fernandez, in the Retention test by ED XRF equipment, of the Preserved Wood Quality Control Laboratory—Universidad del Bío-Bío.

Conflicts of Interest: The authors declare no conflict of interest.

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