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NANO-SUSTAINABLE PROTECTIVE SYSTEM TO CONTROL BIOLOGICAL COLONIZATION FOR WOOD HERITAGE

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Abstract

Wood is highly susceptible to the damaging effects of biological agents. Consequently, there is a growing interest in protecting wood and wood artworks using environmentally friendly preservatives. The objective of this paper was to study the effectiveness of a nano/siliconate impregnation system for wood protection against wood decay fungi. The study was conducted on samples of Pinus ponderosa. The modifiers or protective agents used included siliconates and nanoparticles. The impregnating agent was applied using a brush, treating the solution as a wood stain. To analyze the protective capacity of the treatment against biodeterioration, the decay resistance test was conducted by exposing the samples to two fungal species, brown rot and white rot, for 16 weeks. The results showed that wood treated with nano/siliconate exhibited excellent resistance to decay. It is worth mentioning that synergistic effects were observed when siliconate and nanoparticles were mixed. Additionally, the impregnant was easy to apply, making it suitable for use on various wood objects and providing the necessary versatility for the protection of heritage wood.

Keywords*: Siliconate; Nanometals; Wood; Protection*

Introduction

The biodegradation of wood and wood products caused by fungi is recognized as one of the most significant problems worldwide, especially when it comes to heritage objects. Their actions can lead to potential historical losses. As a result, there is a growing interest in the conservation of wood and wood artworks, with a focus on using environmentally friendly preservatives [1-4].

Silicon compounds are synthetic molecules widely used in wood protection due to their unique bifunctional structure and specific reactivity [5]. They have been utilized for the preservation and conservation of wood and wood-based products, as well as additives for preservatives, with the aim of improving weathering performance, reducing wood hydrophilicity, decreasing flammability and enhancing decay resistance [6-8]. To achieve more durable wood chemical modification, silicon derivatives (such as isocyanate or epoxy) containing chemical groups capable of forming stable covalent bonds with the -OH groups present in wood polymers may also be applied. Functionalized siloxanes can also be used for wood modification, characterized by a stable and flexible siloxane chain that facilitates proper orientation on the modified surface. Additionally, various functional groups can be attached to

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the siloxane chain, allowing the formation of stable linkages with the substrate and providing specific properties [9-12].

The interaction of nanoparticles with biomolecules and microorganisms is an expanding field of research. Recently, there has been a growing interest in silver formulations as wood preservatives. Copper-based formulations have been widely used for several years, particularly in ground contact applications, to treat wood due to their effectiveness as a biocide and relatively low mammalian toxicity. Several research groups have recently studied nano- and micronized preparations of copper, zinc and silver to enhance wood resistance against fungi and termites. Additionally, some nanoparticles provide resistance against UV radiation, scratches, abrasions and fire properties, among others [13-18].

Therefore, the objective of this paper has been to study the application of two technologies, namely nanoparticles and siliconate, as a wood protective system to enhance resistance against decay fungi.

Experimental part

Materials

The study was conducted on samples of *Pinus ponderosa Dougl. ex C. Lawson*. The cuts had a latewood percentage ranging between 25% and 30%. Before impregnation, the wood samples were dried at 105ºC. The modifiers or protective agents used included siliconates and nanoparticles.

Methods

Impregnant formulation

Nanosilver was synthesized through a chemical process using silver nitrate and sodium citrate as the reducing agent. A solution was prepared by dissolving 0.088g of silver nitrate (1.061mm) in 500mL of water. The solution was then heated to boiling with magnetic stirring at 800rpm. Once the temperature reached 90°C, 10mL of 1% sodium citrate (0.1g/10mL) was added dropwise while maintaining continuous stirring until the solution turned bright yellow. The final dispersion had a concentration of 112ppm.

Nanocopper was also prepared by a chemical process. A solution was made by dissolving 0.156g of Cl_2Cu in 150mL of solution. The solution was then stirred while adding 90mL of a 1.5M sodium hydroxide solution (6g/100mL) as a hydrolysis agent. Glucose (approximately 7g) was gradually added to the solution until it turned yellowish-brown. Stirring was stopped and the solution was placed in a 90°C bath until it turned black (approximately 20 minutes). The final dispersion had a concentration of 324ppm.

The chemical composition of the impregnant was as follows: 1% siliconate (10mL/1000mL; 2.4M postassium methylsiliconate; SILRES BS16; CAS 31795-24-1), 1.6% nanosilver (16mL/1000mL), 0.8% nanocopper dispersion (8mL/1000mL), 70.9% 96° ethanol (CAS 64-17-5; 709mL/1000mL) and 25.7% distilled water (257mL/1000mL).

The impregnating agent was applied using a brush, treating the solution as a wood stain.

(i) The first coats were diluted at 50% with 70/30% alcohol.

(ii) The subsequent two coats were applied at 75% and 100% dilution, respectively.

(iii) Finally, the wood samples were exposed in a chamber under controlled conditions of temperature and humidity (20±2°C and 60±5% RH) for three weeks to allow for gelation and aging (sol-gel).

Decay resistance

Samples treated with the impregnant (sized 20×20×20mm) were exposed to *Coniophora puteana* (brown rot) and *Pleurotus ostreatus* (white rot) for 16 weeks under controlled conditions (25±5 °C and 60-70% RH), following the general guidelines outlined in ASTM D 2017. Subsequently, the samples were placed in an oven at 100±3 °C until a constant weight was achieved.

The mass loss percentages were determined using the following equation:

$$WL, \% = [(Wo - Wf) / Wo] \times 100 \quad [1]$$

Where Wo is the weight of the dried sample without exposure to fungi and Wf is the weight of the dried sample after exposure to fungi.

The design of the decay test allowed a comparison of the mass loss between treated and untreated samples. Mass loss, which directly correlates with wood degradation, was employed as a measure of decay resistance. The weights of dried samples were recorded both with and without exposure to decay fungi and relative weights were calculated. The classification of decay resistance was determined according to Standard EN 350-1 (1994), which introduced five durability classes based on the ratio of mass loss of treated samples to untreated control samples. The durability classes are as follows: very durable (ratio ≤ 0.15), durable (ratio > 0.15 to 0.30), moderately durable (ratio > 0.30 to 0.60), slightly durable (ratio > 0.60 to 0.90) and not durable (ratio > 0.90).

Leaching test

The treated wood samples were submerged in water for various durations, ranging from 1 hour to 120 hours. The measurements were taken at regular intervals, starting with hourly measurements for the first 8 hours and then transitioning to measurements taken every 24 hours. The remaining residues in the water were analyzed using UV spectrophotometry, with specific wavelengths determined for each material in the mixture (ʎ300, ʎ380 and ʎ600). The blank sample used for comparison was the impregnant solution diluted in water.

To support the UV measurements, SEM (Scanning Electron Microscopy) images were taken before and after the leaching assay to observe the presence of nanoparticles. Scanning electron microscopy (SEM) was performed on wood. For each impregnated sample, specimens of 5 mm per side were prepared and mounted on stubs to apply a conductive coating using a metallizer. The coating was performed with gold for 30s. Images were taken using a FEI Quanta 200 scanning electron microscope (LIMF, UNLP).

Results and discussion

Decay resistance

The results of the decay resistance test are shown in Figure 1, which illustrates the percentage of mass loss after 16 weeks of exposure to both types of rot. In the case of the untreated samples, all of them exhibited mass loss values exceeding the minimum threshold specified by the standard (20%), thereby validating the decay test.

The treatment applied to the wood resulted in reduced mass loss, indicating that the treatment could effectively protect the wood from fungal degradation. Based on the criteria outlined in Standard EN 350-1 (1994), the ratio of mass loss for the treated wood samples was below 0.15, classifying them as "very durable" wood.

By analyzing the differential weight loss of the control samples based on the species they were exposed to, it is evident that *Coniophora puteana* (brown or cubic rot, which primarily degrades cellulose) has exhibited the highest level of aggressiveness, followed by Pleurotus ostreatus (white rot, which primarily degrades lignin).

In Figure 2, the mass loss of wood samples treated with the impregnant, as well as with each individual active agent of the impregnant, was depicted. It was observed that when the active agents were used together in the impregnant, the mass loss of the wood samples was significantly lower compared to when the active agents were used individually. This observation indicates a synergistic effect between the active agents.

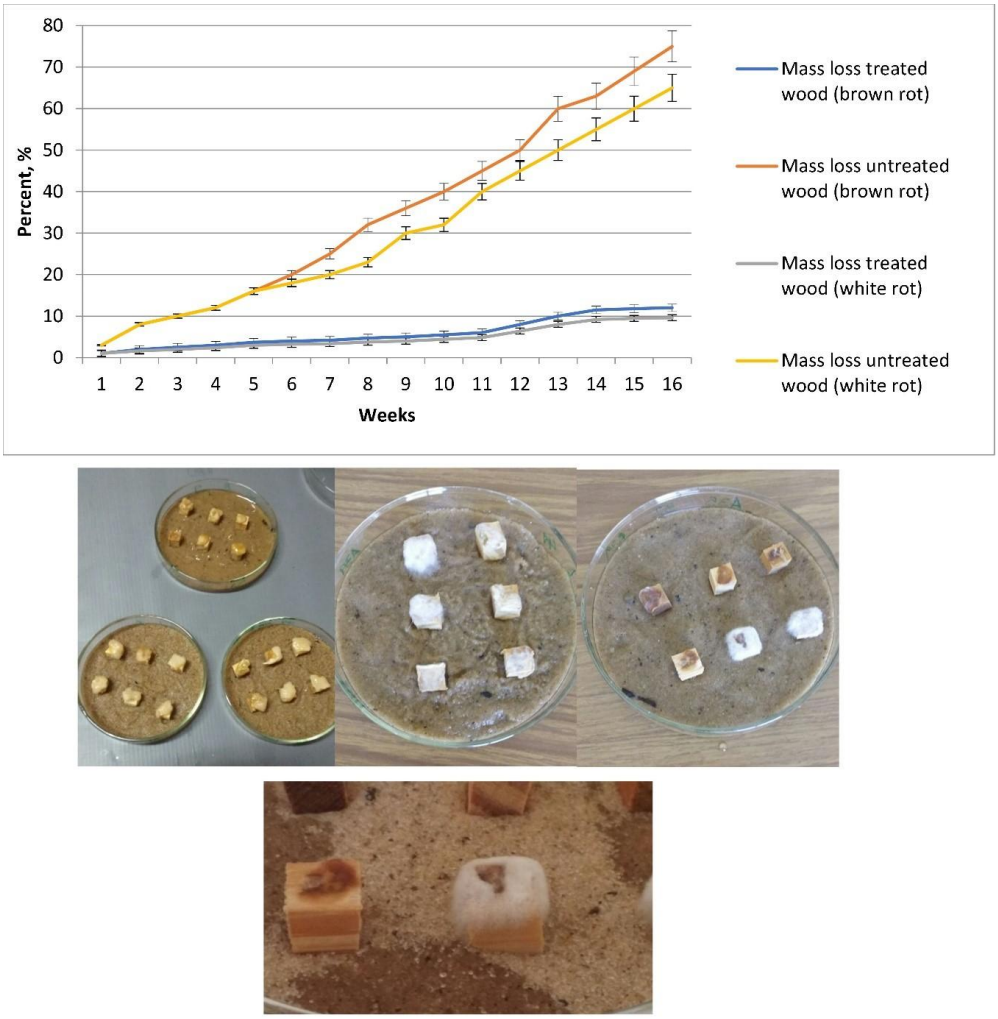

Fig. 1. Decay resistance test

The synergistic effect suggests that the combination of the active agents in the impregnant has a stronger protective effect against decay than when the agents are used alone. This synergy may be attributed to the complementary mechanisms of action of the active agents, which enhance the overall effectiveness of the impregnant in preventing wood decay.

Overall, the results shown in Figure 2 highlight the importance of using a combination of active agents in the impregnant for achieving improved protection against decay, as compared to using individual agents alone.

Leaching

The results of the leaching test are crucial in assessing the potential environmental impact and residual toxicity risks associated with the impregnant. The absence of migration or leaching of the impregnant or its active components into the water throughout the test duration is a positive finding.

The SEM images show the presence of nanoparticles before and after the leaching test (Fig. 3).

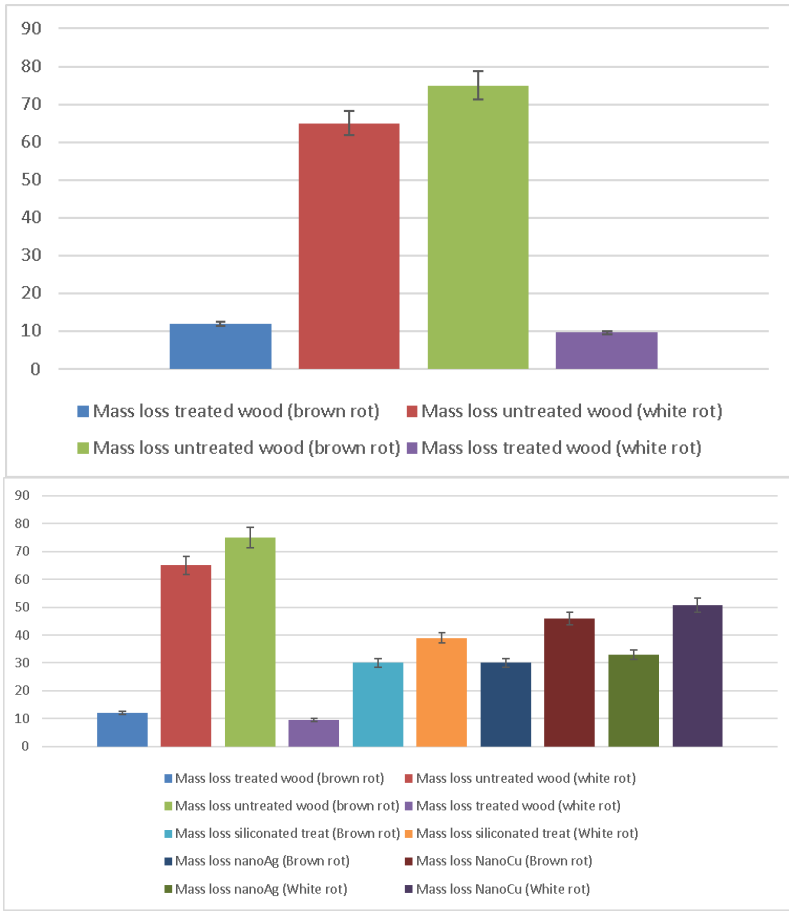

Fig. 2. Synergic effect of treatment

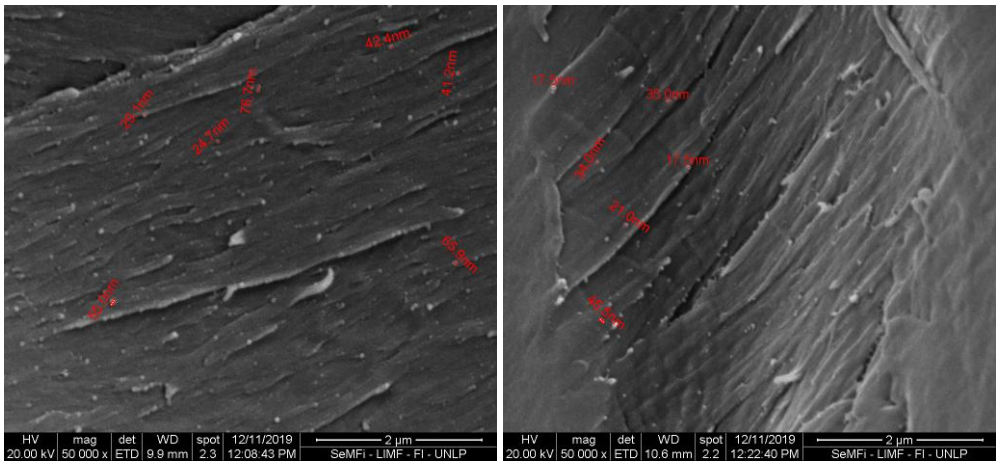

Fig. 3. SEM of treated wood after (up) and before (down) the leaching test

Both results indicated that the impregnant used in the study did not release any significant amounts of toxic substances into the surrounding environment. The lack of leaching suggests that the impregnant remains bound within the wood matrix.

Based on the information provided, it could be concluded that the chemical modification occurred in different layers of the cell wall, with the variety of rot being determined by the polymer that the fungi attacks. This can be attributed to the interaction between the impregnant and the cell wall components during the hydrolysis and condensation reactions of the sol-gel process, resulting in the formation of a non-occlusive coating on the wood. The formation of a polymerized layer within the cell wall can create a steric hindrance, physically blocking the access points that fungal enzymes require to degrade and grow within the wood [22-25]. This hypothesis is supported by the following observations:

(i) During the impregnation process, the water-repellent substances (siliconate and nanoparticles) are carried by the alcohol and water and deposited on the wood surface, where polymerization occurs through the sol-gel process.

(ii) The alcohol evaporates during the formation of the xerogel film, which occurs during curing and aging.

(iii) The formation of the coating is not uniform and occurs in certain areas surrounding non-coated regions. In other words, the coating is formed around clusters of cells, leaving an untreated core.

This explanation accounts for the effective protection of the wood, even when low levels of impregnant are used.

Indeed, in this study, the nanoparticles used in combination with siliconate could be acting as an anchorage, enhancing the wood's chemical modification. The presence of nanoparticles not only contributes to the overall protective effect but also provides additional benefits through their intrinsic properties.

Firstly, the nanoparticles can facilitate the chemical modification of the wood cell wall by serving as anchor points for the siliconate molecules. This improves the adhesion and penetration of the siliconate into the wood structure, resulting in a more effective and durable modification of the cell wall components.

Secondly, the nanoparticles themselves may possess biocidal properties, which further contribute to the protection of the wood. The nanoparticles can inhibit the growth of microorganisms, such as fungi and molds, thus preventing decay and surface contamination. This dual mechanism of action, involving both the chemical modification of the wood and the biocidal effect of the nanoparticles, confirms the performance and effectiveness of the treatment (synergic effect). This approach provides a comprehensive and multifaceted protection strategy for wood preservation, ultimately improving its durability and extending its lifetime.

Finally, the absence of leaching is important for evaluating the environmental safety and sustainability of the impregnation treatment. It provides assurance that the treatment is not introducing harmful substances into the ecosystem and can be considered as an environmentally friendly option for wood protection. It is worth noting that the absence of leaching observed in this specific study does not guarantee the same outcome for different formulations or conditions. Further research and testing may be necessary to assess the leaching potential of impregnants under various scenarios and to ensure their long-term environmental safety.

Conclusions

In conclusion, the impregnant treatment proposed in this study proved to be an effective technique for the restoration, protection and conservation of heritage assets. It offers several advantages over traditional restoration methods, such as the absence of toxic solvents, no formation of an internal polymer structure and shorter curing time, among others.

One significant advantage of the impregnant treatment is that it does not alter the aesthetics of the wood. This makes it particularly suitable for use as a consolidant for heritage objects, as it allows for the preservation of their original appearance.

The combination of the impregnant with siliconate and nanoparticles resulted in a synergistic effect, enhancing the protective properties of the treatment against biological wood deterioration. This demonstrates the efficacy of combining different treatments to achieve a more efficient and comprehensive protective system.

Overall, the proposed impregnant treatment offers a valuable alternative for the restoration and conservation of heritage assets, providing effective wood protection while considering important factors such as environmental safety, aesthetics preservation and efficiency. Further research and application in the field of heritage conservation are warranted to validate and expand upon these findings.

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