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Improvement of Dimensional Stability, Water Resistance, and Decay Resistance of Pine Wood by the Incorporation of Polyvinyl Chloride-Abietic Acid Copolymer with AgNPs†

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Abstract: In this study, Abietic acid (Aba), polyvinyl chloride (PVC) and nano silver (AgNPs)were blended by mixing and dissolving in tetrahydrofuran. Pine (*Pinus sylvestris*) sapwood were impregnated with the PVC-Aba-AgNPs under vacuum in a small-scale impregnation container. The weight percent gain, density, water absorption, swelling properties, and decay resistance of the treated wood were measured in detail. PVC-Aba-AgNPs treatments decreased the swelling properties and water absorption of wood, but increasing the anti-swelling efficiency (ASE) to approximately 12% after 8-day immersion in water. Mostly, the treated samples were found to be more resistant to decay compared to the control. Unleached and leached test samples showed the same mass loss after fungal decay tests.

Keywords: abietic acid; polyvinyl chloride; nano silver; wood; decay test; physical properties

1. Introduction

Wood is a composite made of three main polymers (cellulose, lignin and hemicellulose) that can be broken down by various microorganisms. The most important microorganism that destroys wood is fungi. Decay fungus are important to nature. However, it degrades the structure of the wood and shortens its service life. While some woods are naturally resistant to rot, some woods have a very low natural resistance to rot. For this reason, various methods are applied to increase the service life of wood.

The packaging of foods plays an important role in the preservation of the product throughout the storage and distribution chain. The main purpose of packaging is to protect food from contamination and extend its shelf life [1]. Many materials are used in the production of packaging materials and polyvinyl chloride (PVC) is one of the most used materials. PVC materials are easily processed with thermoplastic methods. It is also very popular due to its non-flammability, dimensional stability, high resistance to weathering and low cost [2]. However, most of the research has focused on environmentally friendly and biodegradable polymers due to environmental concerns and renewability [3–7].

Abietic acid (Aba), is a resin acid and are liberated from wood during pulp manufacturing processes [8] from *Pinus contorta* (lodgepole pine), *Abies grandis* (grand fir). Abietic acid derivatives have various due to their low cost, biocompatibility, biodegradable, and chemical modification capability [9,10]. It has also been suggested that silver nanoparticles should remain in a matrix for antimicrobial application, and the resin is suitable for this

[11], antiallergic [12] and air filter for indoors or antibacterial filler for wooden furniture [13]. It also provides good hydrophobic properties as it has a partially unsaturated compound with a carboxyl group and three fused six-membered rings [14]. In recent years, studies related to the incorporation of metallic nanoparticles (NPs) into the polymeric structure have attracted attention. Polymeric matrix can significantly increase the stability of nanoparticles [15–17]. However, to our knowledge, there are no reports on the silver nanoparticles in the abietic acid polymer in wood that has been treated with silver-abietic acid formulations.

Silver nanoparticles (AgNPs) have antimicrobial and antifungal properties because of their small size and increased surface area [18,19]. The most important of these is that AgNPs can inhibit fungi at low concentrations and these levels do not have a toxic effect on human cells [20]. The effects of AgNPs against different kinds of fungi in wood have been reported by a lesser number of researchers. One of the first studies on the use of AgNPs as a biocide in wood protection was carried out by Dorau [21]. High colloidal and ionic silver activity has been observed against microbes with AgNPs impregnation. It has been reported that AgNPs in different concentrations are effective against *Candida albicans* and *Saccharomyces cerevisae* and destroy fungal cells [22]. Another study found that impregnation of wood with 200 and 400 ppm AgNPs was effective against the white rot fungus *Trametes versicolor*. AgNPs could not completely inhibit fungal growth. However, the fungus significantly reduced weight loss at the end of the test [23]. In another study, it was stated that 1000 ppm and 3000 ppm AgNPs material against brown rot fungus did not prevent the development of *Poria placenta* fungus, but reduced it [24].

2. Materials and Methods

Pine (*Pinus sylvestris* L.) wood samples with a density of 0.42 g/cm^3 were used in this study. All samples were taken from the sapwood part and cut in dimensions of 20 (Radial, R) x 20 (Tangential, T) x 10 (L, Longitudinal) mm^3 for the leaching tests and 5 (R) x 15 (T) x 30 (L) mm for the decay test. The $AgNO_3$, polyvinyl chloride (PVC), and tetrahydrofuran (THF) were supplied by Sigma-Aldrich (Germany).

The distribution of abietic acid in the polymer was investigated according to the relevant reference [25]. The addition of silver into the polymer was done according to the literature [26]. Both the mixture of 5g abietic acid/15g PVC and 10g abietic acid/10g PVC were dissolved in 100 mL of THF, in order to prepare two stock solutions before impregnation. 1g AgNPs was added to these prepared stock solutions. Impregnation was achieved using the procedure reported in our recent article [27]. Before and after impregnation, wood samples were kept at 103 °C until they reached full dry weight. While the wood samples were completely dry, they were impregnated with PVC, PVCAba, PVCAba-AgNPs solutions. The impregnation of wood samples was carried out under vacuum (650 mmHg) for 1 h and under atmospheric pressure for 1 h. The WPG (weight percentage gain) for each samples was calculated based on the initial (Wu) and final (Wt) weight of each wood sample using Eq. (1).

$$WPG1(\%) = 100[(Wt - Wu)/Wu] \quad (1)$$

where Wu: untreated (oven-dry weights) and Wt are treated wood (oven-dry weights) blocks.

2.1. Examination of the Physical Properties of Wood

In the study, physical properties of wood such as water absorption (WA), swelling coefficient (S), anti-swelling efficiency (ASE), and mass loss by leaching were investigated according to the relevant standards [28].

2.2. Leaching and Decay Test

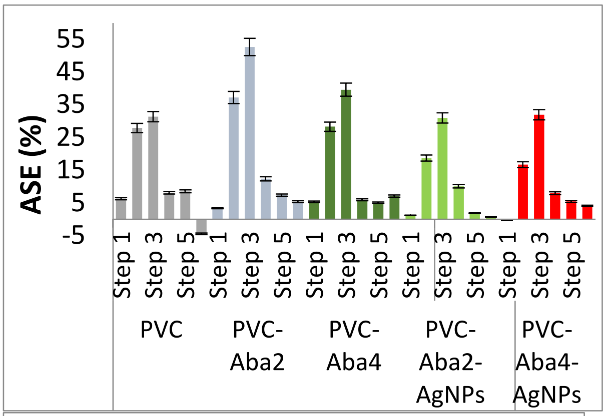
The fungus test of the wood was carried out according to the relevant standard [29,30]. In this study, Coniophora puteana (Mad-515) as a brown rot fungus, and Trametes versicolor (L.) Lloyd (Mad-697) as a white rot fungus, were used.

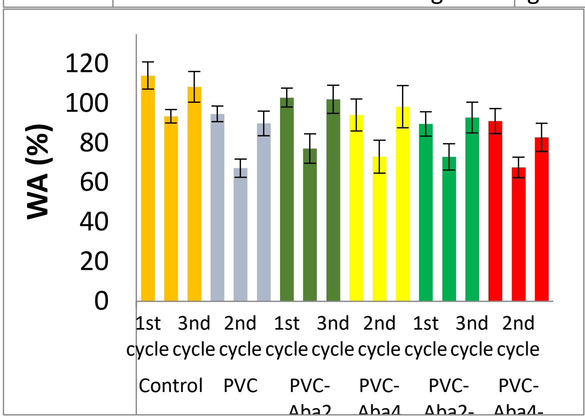
2.3. ATR-FTIR Spectroscopic Analysis

The FTIR spectra of modified (impregnated) and unmodified wood (control) samples were recorded by Shimadzu IR Affinity^{-1} FT-IR spectrophotometer equipped with an attenuated total reflectance probe (Shimadzu Corp., Kyoto, Japan). The measurement was carried out in the range of 400-4000 cm^{-1} with 32 scans at 4^{-1} resolution. The graphics prepared after the test were drawn in the Originlab-2019b program.

3. Results

According to the results obtained, a weight gain value between 1.99% and 4.37% was obtained for the wood samples. The maximum weight gain was obtained at 4.37% in PVC-impregnated samples. The CH_3 bonds in the PVC structure bond with the hydroxyl ends in the wood cell wall. After the modification process, it was leached with THF to remove the PVC material that did not bond with the wood cell wall. In other variations, 3.14%, 2.67%, 3.07% weight gains were obtained for PVC-Aba2, PVC-Aba4, PVC-Aba2-AgNPs, respectively. The least weight gain was obtained with 1.99% in the PVC-Aba4-AgNPs sample group.





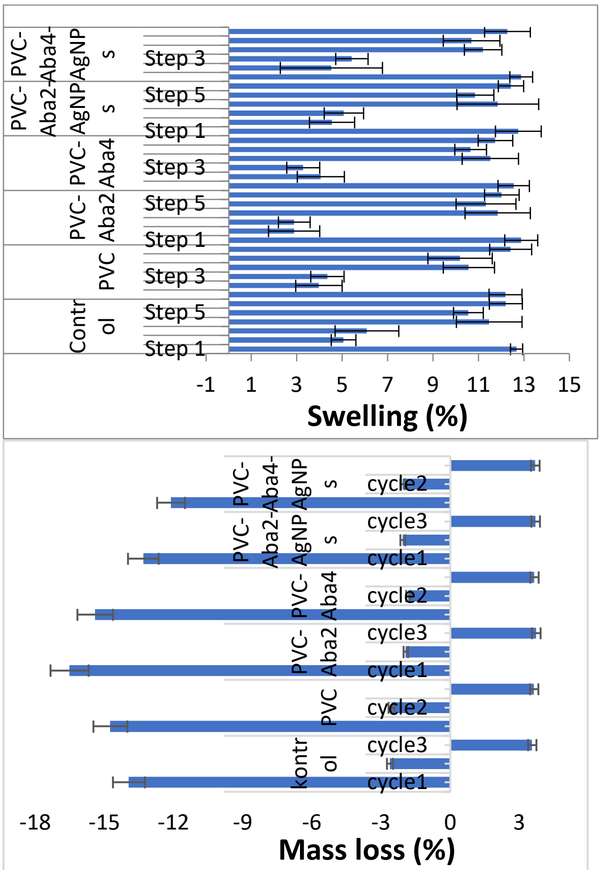


Figure 1. ASE (Average anti-swelling efficiency values %), swelling values, mass loss values by leaching, and water uptake values of untreated and modified samples.

As shown in Figure 1, impregnation of PVC and PVC-Aba inside wood improves some physical attributes of wood. 30% less swelling and ASE (anti-swelling efficiency) were obtained in the impregnated wood samples. Minimum ASE values were obtained in samples impregnated with PVC and PVC-Aba2-AgNPs. The maximum ASE value was observed in PVC-Aba2 samples. ASE values decreased in parallel with the increase in ASE processing time.

PVC is a polymer with a hydrophobic character. The hydroxyl groups in the wood samples impregnated with PVC are connected by the CH_3 bonds in the PVC end groups and provide a certain amount of water repellency to the wood. In addition, in the literature study, it was reported that filling the wood cell cavities with any polymer would provide water repellency to the wood [31–33]. In the study, it is thought that PVC and PVC-Aba-AgNPs remain in the wood, therefore they provide dimension stabilization to it. In this study, only 1-4% weight gain was obtained in wood samples.

The modification process did not have a positive effect on the swelling values of the wood. Control and test samples exhibited similar behavior. After the water intake test, 10-15% weight loss was observed in the test and control samples. These weight losses are due to the water-leaching compounds, polymers, and silver nanoparticles from the wood.

Figure 2 shows the mass loss values in the control and test samples after the decay test.

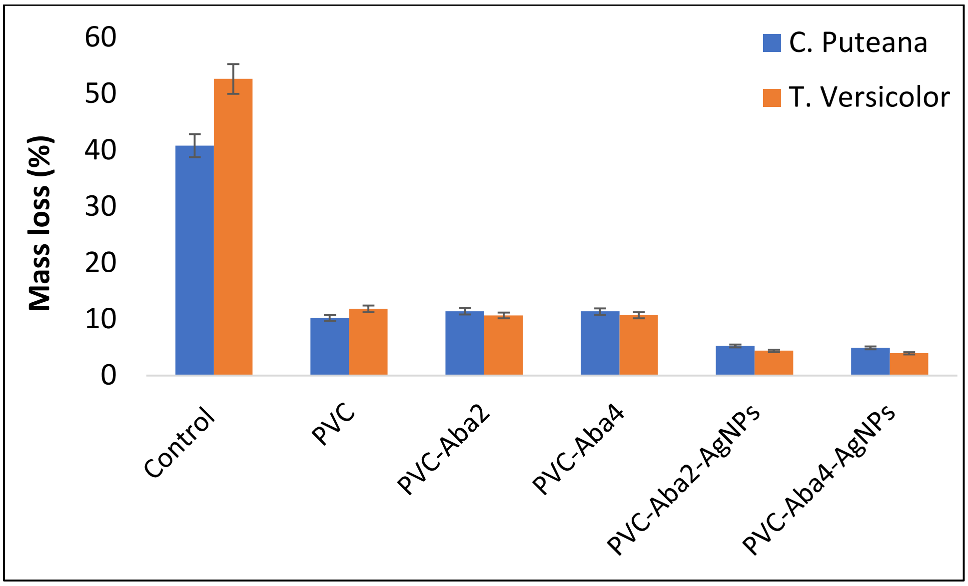


Figure 2. Mass loss (%) of test and control wood after decay test**.**

There was a significant weight loss in the control samples 40.8% and 52.7% according to the eight-week decay test results given in Figure 2. The highest weight loss with 52.7 was obtained in control samples exposed to *T. versicolor* fungus. It is understood that the test is successful because of the weight loss of control samples above the 20% weight loss specified in the standard [30]. Compared to the control samples, 87.0-92.0% less weight losses were obtained in the test samples. The lowest weight loss was obtained in PVC-Aba4-AgNPs samples, and the highest weight loss was obtained in PVC-Aba4 samples. It has been stated in literature studies that silver nanoparticles inhibit fungal growth [27,34]. Again, in these studies, it was stated that the effect of silver nanoparticles against white rot fungi was greater than the effect against brown rot fungi.

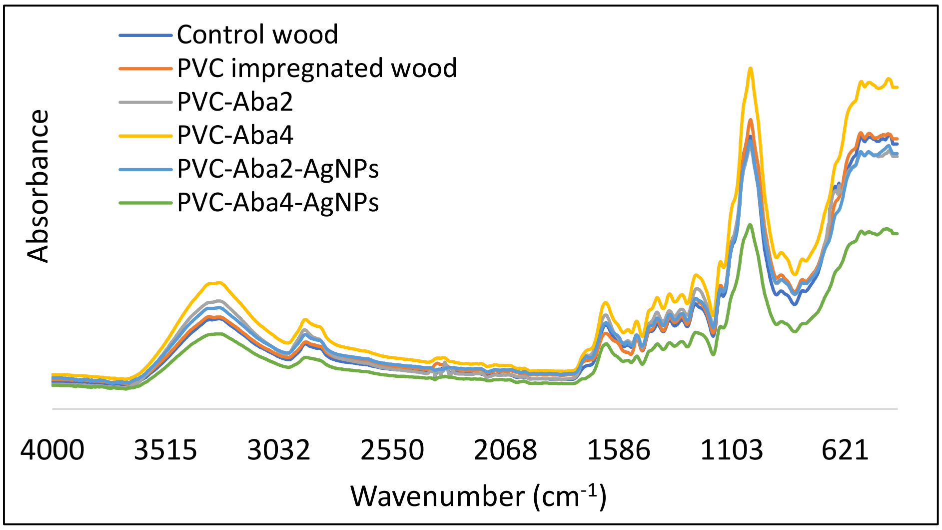


Figure 3. FTIR-ATR spectrum of the wood and impregnated wood**.**

Figure 3 shows the FTIR spectra of the wood samples. It is seen that there are no significant changes in the chemical structure of the wood samples after the impregnation process. It is understood that the impregnation process is not a chemical modification but only an impregnation modification by filling the wood cell.

5. Conclusions

In the study, Abietic acid (Aba), polyvinyl chloride (PVC) and nano silver (AgNPs) were mixed and dissolved in tetrahydro-furan with an environmentally friendly approach, and *Pinus sylvestris* wood samples were impregnated and their physical and biological properties were tested. According to the results obtained, it was concluded that the impregnation process did not improve the physical properties of wood samples, but increase their resistance against both *T. versicolor* and *C. puteana* fungi. Conducting insect and termite tests of PVC-Aba4-AgNPs in future studies will eliminate the shortcomings of the study.

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