Fungal inhibition and chemical characterization of wood treated with novel polystyrene-soybean oil copolymer containing silver nanoparticles

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ABSTRACT

In this study, Scots pine (*Pinus sylvestris* L.) samples were impregnated with autoxidized soybean oil polymer containing Ag nanoparticles (Agsbox) and polystyrene-soybean oil copolymer (AgPSsb) in order to inhibit white-rot fungus (*Trametes versicolor*). Chemical changes of the impregnated specimens were characterized by FTIR techniques. The higher concentration of nano preservative resulted in higher weight percent gain (WPG) in the impregnated samples. The samples impregnated with 1.5% of Agsbox, had the highest WPG (2.98%). The silver nanocomposite-impregnated wood specimens improved the anti-fungal properties. In addition, treatment with 0.4% AgPSsb resulted in the lowest moisture content (23.4%) after decay tests. In the samples, the lowest weight loss (0.87%) due to fungal decay was observed with the use of 0.4 wt% of AgPSsb. Mass losses of Agsbox impregnated specimens at 1.5% and 0.04% were 2.86% and 4.61% respectively. The FTIR spectra of the specimens impregnated with the nanocomposites showed the impregnated components at the peaks of 2910 cm^{-1} and 1714 cm^{-1} in particular.

1. Introduction

In the past and up to the present day, chemical preservatives have been used to protect wood. Copper chromium arsenic (CCA) is a first-generation copper-based wood preservative which is highly effective against a broad spectrum of decay fungi (Bahmani et al., 2015), termites (Lin et al., 2009) and wood-boring insects (Schlultz et al., 2008). Copper chromium arsenic has been replaced by second-generation wood preservatives such as alkaline copper quat and copper azole (Humar and Lesar, 2008) due to the banning of CCA in Europe as well as restrictions on its use in the USA and Canada because of the environmental concerns (Ellis et al., 2007; Kartal et al., 2015).

Environmentally friendly methods (ultrasound, magnetic, microwave and biological methods) and materials (vitamins, sugars, plant extracts, biodegradable polymers and microorganisms) are used in the production of nanoparticles (NPs). Thanks to these techniques, silver, copper, gold, iron, metal alloys and oxides are produced in nano size (Kharissova et al., 2013). In recent years, because of their wide range of applications in diverse fields, NPs such as gold and silver have attracted the interest of chemists (Hazer and Akyol, 2016). In addition, commercial metallic systems either micronized or dispersed as nano

particulates have been studied by several researchers in the last decade (Kartal et al., 2009; Clausen et al., 2010; Mantanis et al., 2014; Huang et al., 2015). For example, nano copper has been used for impregnation of southern pine in the USA and Canada. Nano technological devices have enabled the grinding of metals to sub-micron size and the dispersion of the particles in water (Berrocal et al., 2014; Moya et al., 2017). Inorganic NPs are distributed evenly on the surface, thus increasing their area of influence. With regard to the relationship between NPs and the anatomical features of wood, Matsunaga et al. (2012) found that copper NPs could be distributed within the parenchyma cells, whereas the larger-sized copper particles could be deposited on the wood-cell walls (Matsunaga et al., 2012).

Vegetable oil-based polymers have been attracting the interest of researchers. This interest can be attributed to the biodegradability, low cost and environmentally friendly properties of vegetable oils (Shogren et al., 2004; Xia and Larock, 2010; Lligadas et al., 2013). Earlier works have stated that polyunsaturated plant oils were readily susceptible to autoxidation (Köckritz and Martin, 2008; Soucek et al., 2012; Allı et al., 2016). In order to utilize the free radical polymerization of vinyl monomers, the autoxidation of the double bonds in vegetable oils causes mostly peroxidation and polymerization leading to macro

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peroxide initiators (Allı et al., 2014; Allı et al., 2016; Ince at al., 2016).

In this study, macro peroxide soybean oil with silver NPs was obtained via the autoxidation of soybean oil in the presence of silver nitrate. The silver-soybean oil macro peroxide initiated the free radical polymerization of styrene, resulting in the polystyrene-soybean oil copolymer containing silver NPs.

Therefore, this study aimed to explore the polymerization of silver NPs with soybean oil and polystyrene and to clarify the impact of Ag NPs in the presence of soybean oil on the decay-resistance of treated wood. Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) was used to determine the chemical changes. The structure of the chemical bonds in the impregnated samples was investigated and scanning electron microscopy (SEM) was employed to display the distribution of the Ag NPs. In addition, the impregnated wood specimens were used to investigate the antifungal effects of the soybean oil-Ag and polystyrene-soybean oil-Ag nanocomposites.

2. Materials and methods

2.1. Materials

Scots Pine (*Pinus sylvestris* L.) specimens were prepared from sapwood blocks with the dimensions of $5 \times 15 \times 30$ mm (height × width × length). The oven-dry density of the samples used was 0.42 g cm^{-3}.

The soybean oil was donated by the firm of Çotanak/Altas Yağ Su ve Tarım Ürünleri Gıda Inşaat Otomotiv Nakliyat San ve Tic. A.S., Ordu, Turkey. The oil consisted of palmitic acid (11 wt%), stearic acid (4.9 wt %), oleic acid (34 wt%), linoleic acid (42 wt%) and linolenic acid (3.6 wt%). The AgNO$_3$ was purchased from Sigma-Aldrich.

2.2. Synthesis of soybean oil macro peroxide containing silver nanoparticles (Agsbox)

The autoxidized polymeric soybean oil (PSsbox) was prepared according to the modified procedure for the synthesis of gold nanocomposites reported in our previous work (Hazer and Akyol, 2016).

A mixture of 18 g of soybean oil and 0.52 g of AgNO$_3$ was placed in a Petri dish ($\Phi = 14$ cm, oil thickness: 0.7 mm). This solution was exposed to daylight and air at room temperature. After a given time of autoxidation (ca. 1 month), a sticky, dark-brown, viscous liquid polymer layer was formed. The synthesis of polymeric soybean oil (PSbox) was repeated 10–12 times in Petri dishes having different radii. The resulting nanocomposite contained 2.8 wt% (0.016 mol%) of silver NPs and was designated as Agsbox.

2.3. Synthesis of polystyrene-soybean oil copolymer containing silver nanoparticles (AgPSsb)

Polymerization of styrene was initiated by the oxidized soybean oil polymer with Ag NPs according to the modified procedure described in the cited literature (Hazer and Kalaycı, 2017).

For a typical polymerization experiment, 0.12 g of Agsbox nanocomposite and 4.52 g of styrene were mixed into 5 mL of toluene in a reaction bottle. Argon was introduced through a needle into the tube for about 3 min in order to expel the air. The tightly capped bottle was then put into a water bath at 95 °C for 6 h. The contents of the tube were then coagulated in methanol. The graft copolymer samples were dried under vacuum at 40 °C overnight (Hazer and Kalaycı, 2017). This product was designated as AgPSsb.

2.4. Pretreatment of wood samples

Organic solvent-based solutions including chloroform and toluene were prepared for impregnation of the wood specimens with soybean oil-Ag and polystyrene-soybean oil-Ag NPs. Three different solutions

were used for impregnation of the wood. For this purpose (all w/w): 0.04% and 1.5% of Agsbox were dissolved in chloroform, respectively, and 0.4% of AgPSsb in toluene.

Chloroform and toluene were chosen for preparation of the solutions. Prior to impregnation, the wood samples were pretreated with chloroform and toluene to overcome the possible effect of chemical degradation by the selected solvents in the wood during impregnation. For this purpose, the samples to be impregnated with Agsbox were stirred in chloroform, whereas the samples to be impregnated with AgPSsb were stirred in toluene for 2 h. Afterwards, 2 h of stirring was carried out again after changing the chloroform and toluene. Following the stirring process, the samples were left in the lab for 2 h and then dried in a vacuum oven at 40 °C for 4 h. The samples were subsequently oven dried at 103 °C. Control samples were also left in chloroform for 2 h for comparison with the treated samples.

2.5. Impregnation of wood

Prior to the impregnation, the wood samples were dried in an oven at 103 °C until reaching constant weight. Air-dried samples were treated with dilute solutions in an impregnation chamber according to the full-cell process. In this process, first, samples were left under vacuum at 650 mm/Hg for 30 min, and then followed by atmospheric pressure for 60 min. The weight gain (%) for each compound was calculated based on the initial (Mu) and final (Mt) weight of each wood sample using Equation (1).

$$\text{WPG (\%)} = 100[(Mt\text{-}Mu)/Mu] \tag{1}$$

where Mu and Mt are the oven-dry weights of the untreated and treated wood blocks, respectively.

2.6. Determination of antifungal efficiency

The decay test was performed according to EN 113, but the dimensions of the wood samples were modified to $5 \times 15 \times 30$ mm (height × width × length). Prior to the experiment, wood specimens were dried in an oven at 103 °C until constant weight was reached. *T. versicolor* (L.: Fr.) Pilat white rot fungus was selected for the decay test. Five replicate samples were used for each experiment. The control and treated samples were subjected to conditioning in a chamber at 20 °C and 65% relative humidity prior to the decay test. The eight weeks decay test was conducted in a chamber at 22 °C and 65% relative humidity. At the end of the experiment, weight loss was determined based on the oven-dry weight of the test samples in order to assess the biological durability.

2.7. Instrumentation

The morphological analysis of the bio composites was conducted via environmental scanning electron microscopy (ESEM) (Tescan MAIA3 XMU-SEM), with an accelerating voltage of 5 kV. The radial surfaces of the samples were measured. For enhanced conductivity, the surface of all samples was sputter-coated with gold using a Denton sputter coater.

The FTIR-ATR analysis was carried out with a Shimadzu IRAAffinity-1 spectrometer equipped with a single reflection ATR pike MIRacle sampling accessory. Four accumulated spectra with a resolution of 4 cm^{-1} were obtained for wavenumbers from 700 cm^{-1} to 1800 cm^{-1} with 32 scans for each sample. The measurements were performed in the earlywood section of the wood. Spectra measurements were taken from eight different points.

The Agsbox-toluene solution was dried on a 200-mesh carbon-coated transmission electron microscopy (TEM) grid (Electron Microscopy Sciences, CF200-Cu, USA) for analysis and inspected with a M-2100 (Japan) high-resolution transmission electron microscope (HRTEM) at 200 kV (LaB6 filament). Images were recorded with a