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Role of various nano-particles in prevention of fungal decay, mold growth and termite attack in wood, and their effect on weathering properties and water repellency

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A B S T R A C T

The resistance of Scots pine wood vacuum-treated with nano-particles of ZnO, B_2O_3, CuO, TiO_2, CeO_2, and SnO_2 against decay, mold fungi and subterranean termites was evaluated. Weathering and water absorption properties were also studied. Nano-ZnO only was resistant against leaching, while the other compounds leached out from wood specimens at more than 60% release rates. Mold growth in wood specimens was significantly inhibited by treatment with nano-ZnO and nano-B_2O_3. In Petri dishes, all mold fungi were also inhibited by nano-ZnO and nano-B_2O_3; however, nano-SnO_2 inhibited *Trichoderma harzianum* growth only. Weight loss from fungal attack by the brown-rot fungus was significantly inhibited by all nano-compounds tested, except for leached specimens of nano-B_2O_3 treatments. Considerably higher weight losses were obtained in decay resistance tests by the white-rot fungus; only nano-CuO and nano-SnO_2 were effective against this fungus. Nano-CuO and nano-B_2O_3 treatments produced favorable termite resistance in both weathered and unweathered specimens, while nano-ZnO and nano-CeO_2 resulted in decreased weight loss in specimens exposed to termites. Nano-ZnO was slightly effective in decreasing water absorption. Exposing untreated wood specimens to artificial weathering resulted in significant changes in the chemical structure as determined by FT-IR analysis; however, weathering effect was somewhat decreased by the incorporation of the nano-compounds.

1. Introduction

Nano-particles might be an effective tool for protecting wood against mold, decay and termites. Incorporating such particles into traditional wood protection and preservation techniques produces better penetrability and uniform distribution relative to conventional formulations, as well as high dispersion stability and low viscosity (Blee and Matisons, 2008; Kartal et al., 2009; Clausen et al., 2010, 2011). Thus, nano-particles of copper (Cu), zinc (Zn), boron (B), titanium (Ti), silicon (Si), cerium (Ce), silver (Ag) etc., may be important in the development of the next generation wood protection/modification systems (Blee and Matisons, 2008; Kartal et al., 2009). Kartal et al. (2009) reported that Cu, Zn, and B have been important in the development of preservatives that extend the service life of wood against fungi and termites. Blee and Matisons (2008) reviewed the variety of nano-particles, including TiO_2, ZnO, SiO_2, CeO_2, and Ag that have been used in wood modification either in their pure form or in combination with different additives. Several research groups have recently studied the use of nano-and micronized-preparations of Cu, Zn, and Ag to increase the resistance of wood against fungi and termites (Green and Arango, 2007; Clausen et al., 2010, 2011; Németh et al., 2012; Akhtari and Nicholas, 2013; Filpo et al., 2013; Lykidis et al., 2013; Mantanis et al., 2014).

In addition to the increased resistance some nano-particles bring against UV radiation, scratch and abrasion, fire properties,

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hygroscopicity, and mechanical properties of wood, (Blee and Matisons, 2008; Kartal et al., 2009; Clausen et al., 2010, 2011), nano-particles of Zn-, Ag-, and Ti-oxides have been shown to provide more or less protective activity against algal growth and colonization by mold fungi (Shirakawa et al., 2013). In a study by Kartal et al. (2009), mold fungi were moderately inhibited by nano-ZnO treatment with surfactant, but nano-Cu, nano-Zn/nano–Ag mixture, and nano-B did not significantly inhibit mold fungi. Künniger et al. (2014) showed that nano-Ag-containing commercial coatings did not protect wooden test facades against mold, blue stain and algae, due to the low initial silver concentrations in the coating system.

The objective of this study was to evaluate nano-preparations of Zn, B, Ce, Ti and tin (Sn) particles in terms of their capacity to prevent fungal decay and mold growth in wood and on malt-agar growth medium in Petri dishes. Effects of the nano-particles on termite resistance, water repellency and dimensional stability of wood specimens were also determined. Additionally, weathering properties of wood treated with the nano-particles were studied by Fourier-transform infrared spectroscopy (FT-IR) analyses.

2. Materials and methods

2.1. Wood specimens

Specimens were cut from sapwood portions of Scots pine (*Pinus sylvestris* L.) lumber. Wood specimens for the mold resistance, leaching, water repellency, and anti-swelling efficiency tests were 20 mm × 70 mm × 6 mm; those for weathering tests were 135 mm × 45 mm × 3.5 mm. Specimens for fungal decay and termite resistance tests were prepared from the specimens used in weathering tests. The wood specimens (2–4 growth rings cm^{-1}) were free of knots and visible concentrations of resins, and showed no visible evidence of infection from mold, stain, or wood-degrading fungi. The specimens were conditioned to a moisture content of about 12% in a conditioning room at 20 °C ± 2 °C and 65% ± 5% relative humidity (RH) for two weeks before preservative treatments.

2.2. Nano-particle dispersions, solutions and vacuum treatments

The following nano-compounds were tested in this study: nano-ZnO (zinc oxide, <100 nm particle size; Sigma Aldrich Chemistry, USA); nano-B_2O_3 (boron oxide, <30 nm particle size; Düzey Laboratory Chemicals and Appliances, Turkey); nano-TiO_2 (titanium (IV) oxide, <25 nm particle size; Sigma Aldrich Chemistry, USA); nano-CeO_2 (cerium (VI) oxide, <25 nm particle size; Sigma Aldrich Chemistry, USA); and nano-SnO_2 (tin (IV) oxide, <100 nm particle size; Sigma Aldrich Chemistry, USA). In fungal and termite resistance tests, nano-CuO (copper (II) oxide, 23–37 nm particle size; Alfa Aesar, USA) was also tested as a reference chemical.

While dispersions of nano-CuO, nano-TiO_2, nano-CeO_2 and nano-SnO_2 at 1% strength were prepared in ammonia (25%), ethanol (95%) was used for nano-ZnO dispersion at 1% strength. Nano-B_2O_3 solution at 1% was prepared by distilled water.

Wood specimens were vacuum-treated with the dispersions/solution of nano-compounds based on the BS EN 113 standard test method (BS EN, 1997) after the first weights of the specimens were recorded. After treatments, the specimens dry-blotted and weighed again to determine uptake retention levels. Retention levels of the nano-compounds by inductively coupled plasma (ICP) spectroscopy were then calculated as described below. The specimens were then re-dried at 60 °C ± 2 °C for three days.

2.3. Leaching

Half of the treated specimens were subjected to a 14-day leaching course. The leaching procedure was similar to the AWPA E11 standard method (AWPA, 2012). Specimens were placed into a 250 ml bottle, submerged in distilled water, and subjected to a vacuum to impregnate the blocks with the leaching solution. The sample bottles were subjected to mild agitation for a total of 336 h (14 days); the distilled water was renewed after 6 h, and at 1-, 2-, 4-, 6-, 8-, 10-, 12-, and 14-day intervals.

All leached and unleached specimens were then equilibrated at 20 °C ± 2 °C and 65% ± 5% RH for four weeks before mold resistance tests.

2.4. ICP analyses

For the ICP analyses, two leached and unleached specimens from each treatment group were ground to pass a US Standard 40-mesh screen (0.420 mm). Ground wood samples were microwave-digested based on the AWPA A7 standard method (AWPA, 2012), with slight modifications. The samples (~200 mg) were weighed into a microwave digestion tube and nitric acid (8 ml) was added. A digestion blank was prepared along with the samples. The digestion tubes were sealed into digestion vessels and placed in a carousel in a microwave oven for a pre-programmed digestion sequence. After the digestion was complete (20 min), DI-water was added to each vessel to bring it up to 100-ml volume.

The digested samples were analyzed using a PerkinElmer ICP-OES, according to the AWPA A21 standard method (AWPA, 2012), to determine release and retention percentage of B, Ti, Zn, Ce and Sn after leaching. The percent reduction of B, Ti, Zn, Ce and Sn in the treated and leached wood specimens was calculated based on the amount of the elements in the specimens before leaching.

2.5. Mold-resistance tests

Treated and untreated control specimens were evaluated for resistance to mold fungi according to the ASTM D4445-10 standard method (ASTM, 2010) with slight modifications. Three mold fungi, *Aspergillus niger* Tiegh., M-370 (HAMBI 1271, MUCL 28820, ATCC 13496), *Trichoderma harzianum* Rifai, ES 39 (HAMBI 2678) and *Penicillium pinophilum* Hedgc., CEB 3296.31 (HAMBI 2894, DSM 1944, ATCC 36839, CBS 631.66) were grown and maintained on 2% malt agar at 27 °C ± 2 °C, and 80% ± 5% RH. The cultures were obtained from HAMBI – The Culture Collection, Department of Food and Environmental Sciences, Division of Microbiology, University of Helsinki, Finland. A mixed spore suspension of the three test fungi were prepared by washing the surface of individual 2-week-old Petri plate cultures with 10–15 ml of sterile DI water. Washings were combined in a spray bottle and diluted to approximately 100 ml with DI water to yield approximately 3×10^7 spores ml^{-1}. The spray bottle was adjusted to deliver 1-ml inoculum per spray. Specimens were sprayed with 1 ml of mixed mold spore suspension and incubated at 27 °C ± 2 °C and 80% ± 5% RH for four weeks. Following incubation, specimens were visually rated on a scale of 0–5 with 0 indicating the specimen is completely free of mold growth and 5 indicating the specimen was completely covered (0: no growth, 1: 20%, 2: 40%, 3: 60%, 4: 80%, 5: 100% coverage with mold fungi).