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Evaluation of mold, decay and termite resistance of pine wood treated with zinc- and copper-based nanocompounds

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ABSTRACT

In this work, the resistance of black pine wood (*Pinus nigra* L.) vacuum-treated with zinc oxide, zinc borate and copper oxide nanoparticles against mold and decay fungi and the subterranean termites was evaluated. Some of the nanocompounds tested were forced with acrylic emulsions to avoid leaching. Results showed that mold fungi were slightly inhibited by nanozinc borate, while the other nanometal preparations did not inhibit mold fungi. Mass loss from fungal attack by *Trametes versicolor* was significantly inhibited by the zinc-based preparations, while the brown-rot fungus, *Tyromyces palustris* was not inhibited by the nanometal treatments. Notably, nanozinc borate plus acrylic emulsion imparted very high resistance in pine wood to the white-rot fungus, *T. versicolor* with a mass loss of 1.8%. Following leaching, all pine specimens treated with nanozinc borate, with or without acrylic emulsion, strongly inhibited termite feeding, i.e. mass losses varying at 5.2–5.4%. In contrast, the copper-based treatments were much less effective against the subterranean termites, *Coptotermes formosanus*. In general, nanozinc borate possessed favorable properties, that is, inhibition of termite feeding and decay by *T. versicolor*.

1. Introduction

Wood is a heterogeneous and hygroscopic material, which is of lignocellulosic nature and thus is susceptible to biological degradation by fungi, insects and termites. One promising wood protection treatment which has attracted considerable interest from the scientific community during the last decade, is the impregnation of cell wall with nanocompounds (nanometals) with or without emulsions (Clausen, 2007; Matsunaga et al., 2007; Clausen et al., 2010, 2011; Akhtari and Nicholas, 2013; Lykidis et al., 2013). The benefits of applying nanotechnology to wood treatments include the ability of the compounds to have a far greater degree of penetration into the wood (Mantanis and Jones, 2012). It is known that nanoparticles of metals can increase the surface area when evenly dispersed in a layer (Freeman and McIntyre, 2008). In addition, if the particle size is smaller than the diameter of the wood window-like pits (<10,000 nm) or the smallest openings in the bordered pits, i.e. in the margo (400–600 nm) as in the case of pines, complete penetration should be expected and a uniform distribution (Freeman and McIntyre, 2008; Kartal et al., 2009).

In general, copper-, zinc- and silver- based nanocompounds have been used in recent times to enhance the resistance of wood against fungi and termites (Green and Arango, 2007; Cooper and Ung, 2008; Freeman and McIntyre, 2008; Németh et al., 2012; Akhtari and Nicholas, 2013; Lykidis et al., 2013). Clausen et al. (2011) reported a considerable durability enhancement of wood against termites, when impregnated with nanozinc oxide. Németh et al. (2012) showed that spruce, beech and poplar wood impregnated with nanozinc oxide, exhibited a high biological resistance against the brown-rot fungus *Rhodonia placenta*, a particularly tolerant fungus to zinc compounds.

As a matter of fact, nanomaterials possess unique properties and can behave in unpredictable ways (Roco, 2006). Thus, their preparations have several characteristics, e.g. size and charge that may improve their performance in wood protection applications (Clausen, 2007; Mantanis and Jones, 2012). Notably, the commercial use of micronized copper preservatives is currently limited to easily treated pine species because of difficulties in obtaining sufficient penetration in other species. Secondly, the nanoparticles demonstrate high dispersion stability. Fixation of micronized copper is thought to occur mainly through deposition in pit chambers

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and on tertiary cell wall layers rather than via chemical reactions (Freeman and McIntyre, 2008). The addition of a surfactant can further increase dispersion stability by enabling liquid dispersion of higher concentrations of nanometals. Furthermore, the addition of a water-borne acrylic emulsion binder in the compound may increase its affinity to wood polymers and subsequently decrease leaching (Lykidis et al., 2013). In addition, such nanometal preparations have a very low viscosity. Combined, these properties enhance the potential for a much greater penetration into the cell wall as well as a higher protection as a result of the more uniform distribution over the wood surface area.

Nanometal elements like copper and zinc, as well as boron, have played an integral part in the growth of new-generation preservatives responsible for extending the service life of wood products against biological organisms like fungi and termites. The current trend is to diminish or eliminate the use of two common biocides namely arsenic (As) and chromium (Cr) for several wood protection applications because of the potential environmental issues. Copper-based preservatives continue to dominate the market, but even copper as a biocide has come under scrutiny in some countries. Utilizing nanomaterials to create a new generation of novel cost-effective products is a key issue identified by the United States forest products industry (TAPPI, 2005).

The objective of this work was to evaluate the resistance of pine wood vacuum-treated with preparations of zinc- and copper-based nanoparticles, against mold growth, fungal decay by *Trametes versicolor* and *Tyromyces palustris*, and degradation by the subterranean termites, *Coptotermes formosanus*.

2. Materials and methods

2.1. Test chemicals

Chemicals used in the work are shown in Table 1. Three types of nanocompounds were used, namely zinc oxide, zinc borate, and copper oxide, all in combination with two different emulsion binders. The emulsions A and B used are water-borne acrylic polymer emulsions and their characteristics are shown in Table 1. The nanocompounds tested are proprietary formulas, developed by the nanotech company NanoPhos SA (Lavrio, Greece). Two-percent concentrations were prepared based on the metal oxides (i.e., ZnO, CuO). All nanometal preparations were comprised of ∼80 nm particles; their specific size distribution was not available.

2.2. Treatment

A black pine (*Pinus nigra* L.) tree was harvested from a mountainous area of Drama, east Macedonia, Greece, on March 2011, for the research. All test specimens were prepared from the black pine tree's sapwood portions having approx. 5–7 annual rings per cm. The specimens were free of knots and other defects and had no visible signs of infection by wood-destroying organisms. All specimens were pre-weighed and conditioned at 20 °C and 65% RH (relative humidity) for 6 weeks prior to treatment. The average air-dry density of black pine wood was 0.568 g/cm^3. The specimen size varied for leaching, decay, and termite tests according to the AWPA (American Wood Protection Association) E11-97 (AWPA, 2010) and E10-06 methods (AWPA, 2007b), and the Japanese Industrial Standard JIS K 1571 method (JIS, 2010), respectively. Decay and termite specimens were treated with 2% aqueous nanodispersions of test chemicals, in three steps: i) initial 30 min vacuum at 550 mmHg, ii) 5 min vacuum treatment of specimens under vacuum at 550 mmHg, and iii) final 15 min immersion of specimens into the dispersion, under normal climatic conditions. For mold tests, wood specimens were immersed in the nanocompound solutions for a total time of 20 s (ASTM, 1998). Treated specimens were dried at 40 °C for 3 days, weighed, and reconditioned in a conditioning room at 20 °C and 65% RH for two weeks. Differences between the specimen air dry weights (at ∼12% moisture content level), before and after the vacuum treatments were used in order to determine the chemical retention, taking into account the solids content of the nanopreparations.

Table 1
Chemicals tested.

Designation	Test chemical	Type of aqueous acrylic emulsion[a]	Aqueous test solution (%)
A	Zinc oxide	–	2
B	Zinc oxide	Emulsion A	2
C	Zinc oxide	Emulsion B	2
D	Zinc borate	–	2
E	Zinc borate	Emulsion A	2
F	Copper oxide	–	2
G	Copper oxide	Emulsion A	2
H	Copper oxide	Emulsion B	2

Emulsion A: *SurfaPore W* emulsion formulation (NanoPhos SA, Greece)
[a] Emulsion B: Linear acrylic emulsion with TiO_2 (NanoPhos SA, Greece).

2.3. Leaching tests

The leaching procedures were similar to the AWPA standard method E11-97 (AWPA, 2010). One replicate set of five specimens was obtained from each treatment group. Each set of five specimens was placed into a 250 ml bottle, submerged in deionized 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) and renewed with deionized water. Some unleached and leached wood specimens were ground to pass a 30-mesh screen and analyzed for zinc and copper, as well as boron, with inductively coupled plasma (ICP) emission spectroscopy AWPA A21-08 (AWPA, 2007a) to determine retention of nanometals after the leach test.

2.4. No-choice termite resistance tests

A no-choice termite resistance test with the subterranean termites, *C. formosanus* (Shiraki) was performed. Untreated and treated test specimens (20 × 20 × 10 mm) were exposed to *C. formosanus* worker and soldier termites according to the JIS K 1571 standard method (JIS, 2010). An acrylic cylinder (80 mm diameter, 60 mm height), the lower end of which was sealed with a 5 mm thick hard dental plaster (GC New Plastone, Dental Stone; G-C Dental Industrial Corp., Tokyo, Japan), was used as a container. A test specimen was placed at the centre of the plaster bottom of the test container. A total of 150 worker termites collected from a laboratory colony at RISH, Kyoto University, Japan were introduced into each test container together with 15 termite soldiers. The assembled containers were set on damp cotton pads to supply water to the specimens and kept at 28±2 °C and >85% RH in darkness for 3 weeks. The mass loss of the specimens as a result of termite attack was calculated on the basis of the differences in the initial and final dried (60 °C, 3 days) weights of the specimens after cleaning off the debris from the termite attack. Three leached and unleached specimens were tested for each treatment group. The termite mortality rate was calculated by counting the living termites at the end of the tests.

2.5. Mold resistance test

Unleached wood specimens (7 mm tangential × 20 mm radial ×7 cm long) were evaluated for resistance to mold fungi