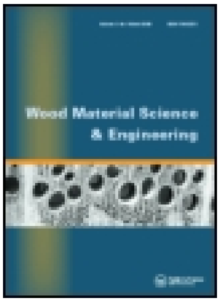

Wood Material Science & Engineering
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/swoo20

Effects of nano-sized zinc oxide and zinc borate impregnation on brown rot resistance of black pine (Pinus nigra L.) wood

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Published online: 16 Sep 2013.

Wood Material Science and Engineering, 2013
http://dx.doi.org/10.1080/17480272.2013.834969

ORIGINAL ARTICLE

Effects of nano-sized zinc oxide and zinc borate impregnation on brown rot resistance of black pine (*Pinus nigra* L.) wood

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Abstract
In this work, the brown rot resistance of black pine (*Pinus nigra* L.) wood, pressure-treated in an autoclave with nano-sized zinc borate and zinc oxide dispersions, was investigated. The two formulations based on zinc borate have given encouraging results, indicating fungicide effects of the metal nanoparticles on *Coniophora puteana*. In specific, mean weight losses for *P. nigra* sapwood exposed to this fungus (one without and one with the addition of a binder) were negligible, that is 0.54% and 0.34%, respectively. On the contrary, the impregnation of pine wood with nano-sized zinc oxide resulted in minimal protection, i.e. 35.9% weight loss. Therefore, nano-sized zinc borate can be utilised in new formulations to impart resistance to wood against the brown rot *C. puteana*.

Keywords: Pinus nigra L., *wood impregnation, nanoparticles, zinc borate, zinc oxide, brown rot,* Coniophora puteana.

Introduction

A significant drawback of using wood in outdoor applications is its susceptibility to biological degradation. One of the most promising protection strategies employed to increase wood durability is the impregnation of cell wall with nanometals (Clausen *et al.* 2010, *Clausen et al.* 2011, Akhtari and Nicholas 2013). Nanometer-size particles of metals can increase surface area when evenly dispersed in a layer. If the particle size is smaller than the diameter of the wood window pit (<10,000 nm) or the opening of the bordered pit (400–600 nm), complete penetration and uniform distribution should be expected (Kartal *et al.* 2009). Among others, zinc-based compounds such as zinc oxide and zinc borate have been used in recent years so as to upgrade several properties of wood, i.e. resistance against weathering, fungi, termites and fire (Manning and Laks 1998, Garba 1999, Clausen *et al.* 2010). Zinc oxide is a well-known, low-cost agent which protects wood from ultra-violet (UV) aging when used in coatings (Weichelt *et al.* 2011). Clausen *et al.* (2011) have reported significant durability improvement against termites of wood impregnated with nano-sized zinc oxide. Németh *et al.* (2013) investigated the antifungal effect of nano-zinc oxide against *Poria placenta*, a brown rot fungus known as a zinc-tolerant organism. Their results showed that nano-zinc inhibited brown rot in the case of spruce, beech, and poplar wood. Zinc borate has been used as an effective compound for improving fire retardancy of wood (Garba 1999). In addition, zinc borate is known for its antifungal and antiinsect properties inherited in wood (Manning and Laks 1998). The objective of this work was to evaluate the effects of impregnation of pine wood with nano-sized zinc oxide and zinc borate against the brown rot fungus *Coniophora puteana*. The addition of a binder in the zinc borate dispersion was also investigated.

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(Received 11 June 2013; revised 31 July 2013; accepted 3 August 2013)

Materials and methods

Wood blocks each measuring 50 × 25 × 15 mm were prepared from mature sapwood of black pine (*Pinus nigra* L.) originating from Pindos mountain in northwest Greece. Pine wood had an air-dry density of 0.59 g/cm^3. All specimens were cut in such a way so that the inclination of the growth rings to the cross section was approximately 45° in order to minimize the effect of the differences between earlywood and latewood on the wood durability. All sapwood specimens, free of defects, were conditioned prior to the treatments at 20°C and 65% relative humidity (RH) for 10 days until constant weight. Three types of dispersions were used, namely zinc oxide, zinc borate, and zinc borate with a binder. The binder used was a water-borne acrylic polymer emulsion. The nano-dispersions were developed by NanoPhos SA (Lavrio, Greece) through the research project no. 3778 (Research Committee, TEI Thessaly). The physical and chemical properties of materials used are shown in Table I.

A series of untreated specimens were also used for comparison. The impregnations were carried out according to the full-cell process in a 1.2 l stainless steel reactor at 26 ± 0.5°C. Specifically, the impregnation process involved an initial vacuum phase at − 0.56 ± 0.01 bar (abs) for 15 min, followed by the transfer of the dispersion to the reactor within 15 s, while vigorously stirred. The filled-up reactor was then pressurized at 6.0 ± 0.1 bar for 60 min. Finally, the blocks were vacuum-treated at −0.56 ± 0.01 bar for 15 min following the removal of the impregnation dispersion. The surfaces of the specimens were then rinsed with water to wash away the residual material and gently dried in a constant climate, at 20°C/90% RH for 84 h, followed by 20°C/75% RH for 84 h, and at 20°C/65% RH for 240 h, until constant weight. The moisture content of the specimens was approximately 12%. The final weight was measured and the retention for each wood specimen was calculated. The decay test was carried out according to the procedure described in EN 113 (1996). Following sterilisation by gamma radiation (25 kGy), the blocks were aseptically inoculated on 4% malt agar in *Kolle flasks* with the brown rot fungus *C. puteana* (BAM Ebw. 15). The Kolle flasks, each of them containing three untreated and three impregnated wood blocks, were incubated at 22°C/65% RH for 12 weeks. Twelve wood blocks per each type of treatment were used in order to determine the mass loss of wood.

Results and discussion

Table II presents the obtained values of retention of pine wood blocks after the pressure treatments, as well as the mass loss of wood following the biological tests. Mean weight loss of *P. nigra* sapwood controls exposed to *C. puteana* was approximately 43.9%, as expected (i.e., >30%). Pine sapwood treated with nano-sized zinc oxide exhibited a mass loss of 35.9%. This decrease in mass loss is not significant.

Notably, dramatic improvements in biological resistance were shown in wood specimens treated with the zinc borate agents. In specific, the zinc borate-impregnated pine wood showed a mass loss of 0.54%, which is in fact negligible. The incorporation of a binder in the zinc borate dispersion proved even more effective; a very low value of mass loss (0.34%) of wood was obtained, but the above differences as compared with the *t*-test are statistically not significant.

In conclusion, such indicative beneficial properties of nano-sized zinc borate (with or without a binder) suggest that zinc borate should be considered in the development of new multi-component wood preservatives. In order to assess the potential in-ground use, further research is needed in order to determine the leaching resistance of such impregnated wood material as well as its biological efficacy over a long period of time.

Table I. Physical and chemical properties of nano-sized zinc-based compounds.

Properties	Zinc oxide (85 nm particle size)	Zinc borate (125 nm particle size)	Zinc borate + binder (particle size: n/a)
Colour	milky white	milky white	milky white
pH	7.6	7.0	6.0
Boiling point	>100°C	>100°C	>100°C
Flash point	>100°C (closed cup)	>100°C (closed cup)	>100°C (closed cup)
Auto ignition point	>100°C	>100°C	>100°C
Density	1.00 g/ml	1.00 g/ml	1.00 g/ml
Viscosity	3 cP (at 25 °C)	4 cP (at 25 °C)	5 cP (at 25 °C)
VOC content	-	-	-
Solids content	2.1% w/w	3.0% w/w	11.0% w/w

Table II. Retention of black pine wood blocks impregnated with nano-sized zinc oxide and zinc borate and mass losses after 12 weeks of *Coniophora puteana* incubation.[a]

Treatment type	Retention (kg/m^3)	Mass loss (%)
Control	–	43.9 (3.4)
Zinc oxide	15.38 (0.32)	35.9 (4.7)
Zinc borate	17.91 (0.43)	0.54 (0.10)
Zinc borate + binder	30.65 (6.01)	0.34 (0.10)

[a]Mean values and standard deviations are in parentheses.

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