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BRIEF ORIGINAL

Biological resistance of pine wood treated with nano-sized zinc oxide and zinc borate against brown-rot fungi

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Abstract In this work, the biological resistance of Scots pine (*Pinus sylvestris* L.) wood impregnated with nano-sized zinc oxide and zinc borate against the fungi *Daedalea quercina*, *Poria placenta* and *Serpula lacrymans* was evaluated. It can be concluded that nano-sized zinc oxide inhibited the biological degradation of pine wood against *Serpula lacrymans*, while it was ineffective against the brown-rot fungus *Poria placenta*. Pine wood treated with nano-sized zinc borate exhibited higher biological resistance against the fungi *Serpula lacrymans* and *Poria placenta*.

1 Introduction

Wood is a hygroscopic material which, because of its lignocellulosic nature is susceptible to biological degradation by several micro-organisms such as fungi. Brown rot in wood is caused by basidiomycetes that attack mainly the hemicelluloses and amorphous cellulose in the cell wall. They can aggressively colonise the wood structure thus resulting in considerable mass losses. To inhibit the fungal attack of wood, a variety of chemical agents have been used successfully for a long time. However, some of those have been recently banned due to health and environmental issues. As a result, the development of environmentally friendly wood-protecting agents with low toxic impact has obtained great attention (Clausen et al. 2011; Shabir Mahr et al. 2013; Lykidis et al. 2013) and is probably going to obtain more in the future.

One of the promising protection techniques applied to enhance wood durability is the impregnation of its cell walls with nano-sized zinc compounds like zinc oxide and zinc borate. Several results have already been published regarding the increase in wood resistance against termites and rot fungi when treated with nano-ZnO and nano-ZnB (Manning and Laks 1998; Clausen et al. 2011; Németh et al. 2013). Among the benefits of applying nano-sized agents to the wood cell wall is the ability to achieve a greater degree of penetration into the cell wall (Kartal et al. 2009). Moreover, if the particle size is smaller than the diameter of the window-like pits (<10,000 nm) or the smallest openings in the bordered pits, i.e. in the margo (400–600 nm), full penetration as well as uniform distribution can be expected (Kartal et al. 2009). In consequence, Németh et al. (2013) have shown that spruce, beech and poplar wood impregnated with nano-ZnO exhibited high biological resistance against the brown-rot fungus *Poria placenta*, a particularly tolerant fungus to zinc compounds.

The objective of the work was to evaluate the effects of impregnation of Scots pine wood (*Pinus sylvestris* L.) with nano-ZnO and nano-ZnB against the brown-rot fungi *Daedalea quercina* and *Poria placenta*, both recommended in EN113 standard (European Committee for Standardization 1997) as well as the dry rot fungus *Serpula lacrymans*.

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2 Materials and methods

Test specimens with dimensions of 50 × 25 × 15 mm^3 (longitudinal × radial × tangential) were prepared from mature sapwood of Scots pine with a mean air dry density of 0.49 ± 0.02 g/cm^3. All specimens were defect-free and cut in such a way that the inclination of the growth rings to the cross section was ~45° in order to minimise the effect of the variability between earlywood and latewood. Prior to the treatments all specimens were conditioned at a temperature of 25 °C and relative humidity of 65 ± 0.5 % until equilibrium was reached inside a desiccator and over a saturated solution of $NaNO_2$. The climatic conditions were recorded with a Vaisala HM333 humidity and temperature transmitter. After conditioning, each specimen was weighed to acquire their initial weight. A series of untreated wood specimens was used as controls (Fig. 1).

For the impregnation of wood, two types of aqueous dispersions were used, namely nano-ZnO and nano-ZnB. Both dispersions were reinforced with an aqueous acrylic polymer emulsion. The dispersions are proprietary formulas of NanoPhos S.A. (Lavrio, Greece). The dispersions were climatised at 25 °C prior to their use. Two percent emulsion solutions were prepared based on the metals (ZnO, ZnB). The nanocompounds were comprised of particles with dimensions of 60–80 nm. Their specific size distribution was not available.

The impregnation was carried out according to the full-cell process in a 1.2 l stainless steel reactor at 25 ± 0.5 °C. The impregnation process involved an initial vacuum phase at −0.94 ± 0.01 bar (g) for 15 min followed by the transfer of the dispersion to the reactor within 15 s, while vigorously stirred using a magnetic stirrer at 1000 rpm. The filled up reactor was then pressurised at 6.0 ± 0.2 bar for 60 min. Finally, the blocks were vacuum treated at −0.94 ± 0.01 mbar for 15 min following the removal of the impregnation liquid. The surfaces of the specimens were then gently rinsed with water to wash away residual material and the specimens were re-conditioned at a temperature of 25 °C and a relative humidity of 65 ± 0.5 % for 20 days. Consequently, the final weight was measured and the weight per cent gain (WPG, %) for each specimen was calculated. The difference of mass loss between each treated/non treated pair was also calculated.

The biological resistance of the wood specimens was assessed by determining the loss in mass caused by fungal attack from brown-rot fungus *Poria placenta* as well as dry rot fungus *Serpula lacrymans*, according to the method described in EN113. The experiment was performed with five replicates per fungus/dispersion. Each replicate consisted of a flask containing one treated and one untreated specimen. Statistical comparison of means was executed with ANOVA (α = 0.05) using SPSS 18.0.

3 Results and discussion

From Table 1 it can be concluded that mean weight per cent gain values occurred by the impregnation varied between 3.5 and 3.9 % for nano-ZnB and between 3.5 and

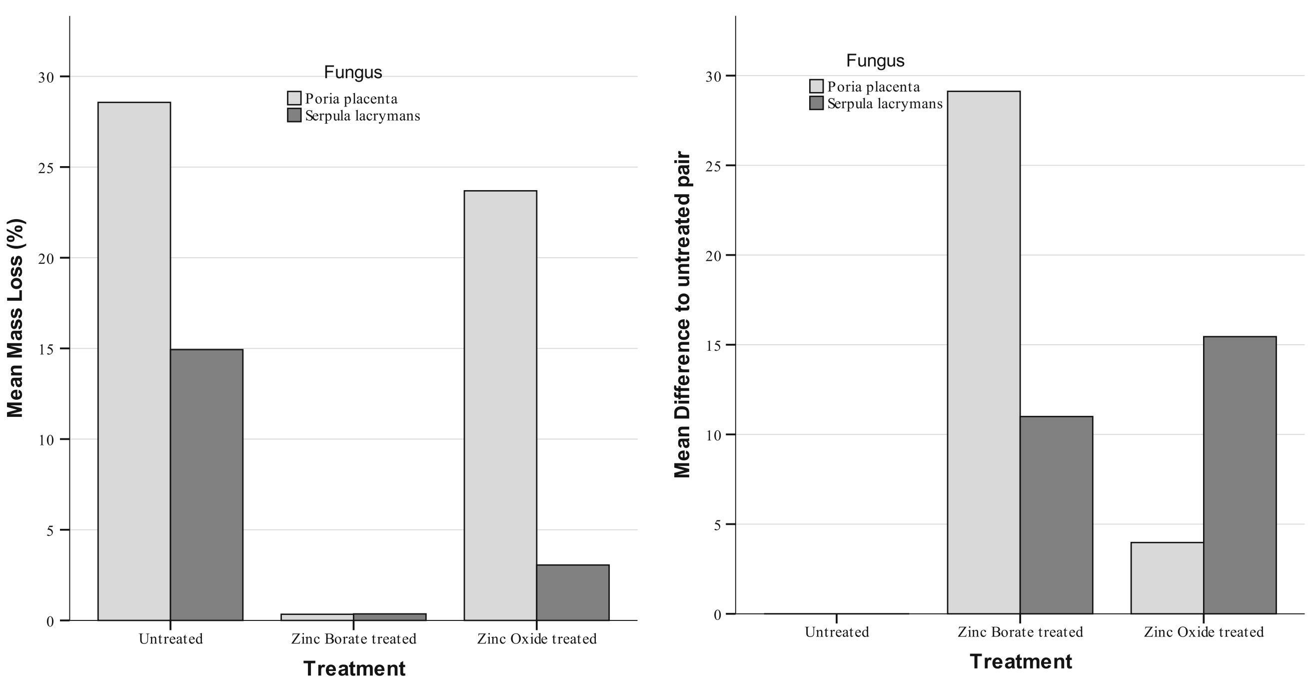

Fig. 1 Mean values of mass loss (ML) and ML difference compared to untreated pair for the specimens of this work

Table 1 Mean values and standard deviations of ML, ML difference to untreated pair, density and WPG for the specimens used in this work

Treatment	Fungus	
	Poria placenta	Serpula lacrymans
Control		
Mass loss (%)	28.56 (5.944)	14.93 (13.230)
Mass loss difference to untreated pair (%)	–	–
Density (g/cm^3)	0.51 (0.05)	0.50 (0.03)
WPG (%)	–	–
Nano-ZnB		
Mass loss (%)	0.34 (0.264)	0.36 (0.235)
Mass loss difference to untreated pair (%)	29.12 (8.15)	11.00 (10.62)
Density (g/cm^3)	0.50 (0.04)	0.49 (0.05)
WPG (%)	3.8 (1.6)	3.5 (0.8)
Nano-ZnO		
Mass loss (%)	23.69 (3.156)	3.06 (5.281)
Mass loss difference to untreated pair (%)	3.97 (4.12)	15.45 (18.49)
Density (g/cm^3)	0.49 (0.03)	0.47 (0.02)
WPG (%)	3.5 (0.6)	4.4 (1.4)

Standard deviations in parentheses

4.4 % for nano-ZnO treated specimens and that, obviously due to the uniform size distribution of nano-particles used, there were no statistically significant differences among these values, for each separate treatment used.

Mean mass losses induced by decay for control and treated pine wood are also shown in Table 1. As expected, untreated pine wood exhibited low biological resistance against *Poria placenta* presenting mass loss of 28.6 %.

It was noted that the brown-rot fungus *Poria placenta* was not inhibited by the nano-ZnO treatment, i.e. mass loss of 23.7 %. In contrast, the treatment with nano-ZnB proved very effective because the treated pine wood showed an almost negligible mass loss (0.3 %). This finding is similar to that found by Lykidis et al. (2013) regarding zinc-oxide treatment of wood, against the brown-rot fungus *Coniophora puteana*.

In addition, it can be concluded that nano-ZnB significantly improved the biological resistance of pine wood against *Poria placenta* and *Serpula lacrymans*.

Nano-ZnO improved the durability of Scots pine wood against all three tested fungi but, compared to non-treated wood, mean mass loss values were significantly reduced (from 14.93 to 3.06 %) only in the case of *Serpula lacrymans*. The mean mass loss difference between control and treated pine wood against *Poria placenta* was only 3.97 % indicating a high resistance of *Poria placenta* against nano-ZnO.

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