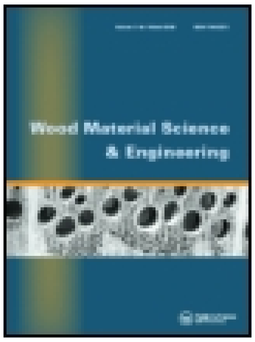

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ORIGINAL ARTICLE

Termite resistance of beech wood treated with zinc oxide and zinc borate nanocompounds*

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ABSTRACT
The field of wood protection is currently changing due to the restrictions imposed by the Biocidal Products Regulation. The need for development of new wood protection technologies is therefore growing. In this work, the resistance of European beech (*Fagus sylvatica* L.) wood impregnated with nano-dispersions of zinc oxide (nano-ZnO) and zinc borate (nano-ZnB) against the termite *Reticulitermes grassei* Clement was investigated. Three different concentrations (0.5%, 1%, 2%) of the nanocompounds were tested. The effects of water leaching were also investigated. A severe effect in terms of termite workers mortality was induced by both dispersions, even at the lowest concentration. In terms of termite feeding, nano-ZnO dispersions appeared to be more efficient than nano-ZnB as they induced significant improvement at concentrations as low as 0.5%. Nano-ZnB was applied at 1% or higher concentrations in order to impart similar changes. Nano-ZnB dispersions were efficient in terms of termite resistance for a concentration at least 1%. Further increasing concentration to 2% resulted in a respective increase of wood efficacy against termites. For both tested nanocompounds, water leaching did not result in any significant increase of termite feeding.

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KEYWORDS
Wood resistance; termite; nano-zinc oxide; nano-zinc borate; impregnation

Introduction

The introduction of nanotechnology in the field of wood has provided opportunities to a wide range of potential applications. Among the most important of them is the use of nano-sized metals for the improvement of physical and biological properties of wood. Nano-sized metals are very effective in wood protection mainly because, due to their size, they can increase the effective surface area in an evenly dispersed layer (Freeman and McIntyre 2008). Moreover, these particles due to their size can penetrate through the cell wall openings and provide much higher retention resulting to a higher biological durability of wood (Kartal *et al*. 2009).

Nano-zinc oxide (nano-ZnO) and nano-zinc borate (nano-ZnB) are well-known examples of nano-sized metals used for improving some properties of lignocellulosic materials. Nano-ZnO has been widely used as wood coating additive for the enhancement of ultraviolet (UV) stability and biological resistance (Hegedus *et al*. 2008, Lowry *et al*. 2008, Lei *et al*. 2010, Weichelt *et al*. 2010, Yu *et al*. 2010, Auclair *et al*. 2011, Saha *et al*. 2011, Farahani and Banikarim 2013). Nano-ZnB has been utilised as an effective compound for upgrading the flame retardancy (Garba 1999) as well as the fungicidal and insecticidal properties of wood (Manning and Laks 1998).

Almost all of the above-mentioned work was related to the use of nano-ZnO and nano-ZnB for the surface protection of wood, while until recently there was not so much information available about their efficiency when impregnated in wood. During the last few years, efforts in this field have been undertaken in order to enhance the durability and service life of wood (Kartal *et al*. 2009, Clausen *et al*. 2010a, Mantanis and Jones 2012, Akhtari *et al*. 2013, Lykidis *et al*. 2013, Németh *et al*. 2013, Mantanis *et al*. 2014). Clausen *et al*. (2010b) reported that nano-ZnO impregnated wood inhibited fungal decay to some extent, except for fungi that are zinc-tolerant (e.g. *Postia placenta*). They found that impregnation of wood with nano-ZnO inhibited termite feeding and caused moderate termite mortality and inhibition. In addition, they noted almost no leaching in nano-ZnO impregnated pine wood specimens after a laboratory test (Clausen *et al*. 2010a). They also reported that, after 12 months of outdoor exposure, significant UV protection was achieved; noticeably, a high chemical depletion was shown for specimens treated with high concentrations of nano-ZnO. Furthermore, impregnation with nano-ZnO dispersion having concentration higher than 2.5% provided substantial resistance to water absorption following 12 months of outdoor exposure, as compared to untreated and unweathered pine wood. Later on, the same scientists reported high leaching and termite resistance of pine wood impregnated with nano-ZnO at concentrations up to 5% (Clausen *et al*. 2011). Both leachability and termite resistance were not influenced by the nano-ZnO particle dimensions. Mass loss of wood by eastern subterranean

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termites was less than 4%, and their mortality was greater than 94%.

In addition to the above, Németh *et al*. (2013) reported that nano-ZnO inhibited brown rot by *Poria placenta* in the case of spruce, beech, and poplar wood. Akhtari *et al*. (2013) studied the spectra of wood specimens impregnated with nano-ZnO, concluding that there were not observed significant changes in lignin and carbohydrates after exposure to *Trametes versicolor* indicating fungicide effects of the ZnO nanoparticles. Lykidis *et al*. (2013) investigated the brown rot resistance of black pine wood (*Pinus nigra* L.) pressure-treated in an autoclave with nano-ZnO and nano-ZnB dispersions. Mean weight losses for *P. nigra* sapwood exposed to *Coniophora puteana* were ca. 0.6% when treated with nano-ZnB. On the contrary, impregnation of pine wood with nano-ZnO resulted in less durability (weight loss of 35.9%) against the same fungi.

In view of the fact that information about the durability of nano-ZnO and nano-ZnB impregnated wood against wood boring insects is limited, purpose of this work was to contribute by assessing the biological resistance of European beech wood treated with the forementioned particles against the termite *Reticulitermes grassei*.

Materials and methods

Materials

Wood block tests with dimensions of 25 × 25 × 15 mm, free of defects were prepared from mature, air-dried sapwood of European beech (*Fagus sylvatica* L.).

Nano-ZnO and nano-ZnB dispersions at three concentrations (0.5%, 1.0% and 2.0%) were used for the impregnation of wood specimens. The nano-dispersions as well as their physical and chemical properties (Table 1) were provided by NanoPhos S.A. (Lavrio, Greece).

The species of termite tested has been *R. grassei* Clement, cultured in chamber under controlled conditions at 28 ± 2°C and 80 ± 5% of relative humidity (RH).

Preparation of samples

All wood blocks were initially dried in a ventilated oven at 103 ± 2°C for 96 h and then weighed to acquire their anhydrous weight (m_0). Afterwards, they were conditioned at 20 ± 2°C and 60% RH for approximately one month until constant weight. The moisture content of the conditioned specimens varied between 9.6% and 9.8%.

Impregnation and leaching

Lab-scale impregnation of wood with the two types of dispersions, namely nano-ZnO and nano-ZnB, was carried out according to the full cell process in a 1.2 L stainless steel reactor. Specifically, the impregnation process comprised 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 loaded reactor was then pressurised at 6.0 ± 0.1 bar for 60 min. Finally, the dispersion was withdrawn and the specimens were vacuum-treated at

Table 1. Physical and chemical properties of nano-sized zinc-based compounds.

Property	Zinc oxide	Zinc borate
Particle size	85 nm	125 nm
Colour	Milky white	Milky white
pH	7.6	7.0
Boiling point	>100°C	>100°C
Flash point	>100°C (closed cup)	>100°C (closed cup)
Auto ignition point	>100°C	>100°C
Density	1.00 g/mL	1.00 g/mL
Viscosity	3 cP (at 25°C)	4 cP (at 25°C)
Solids content	2.1% w/w	3.0% w/w

0.56 ± 0.01 bar for 15 min. The surfaces of the specimens were then rinsed with water to wash away any residual material. Afterwards, they were gently air dried in a constant climate, dried out at 103 ± 2°C for 96 h and were re-weighed in order to get their dry weight after impregnation (m_i). Weight per cent change after impregnation (WC_i) for each specimen was calculated using the following equation.

$$WC_i(\%) = 100 \times (m_i - m_0)/m_0. \quad (1)$$

Leaching with water was carried out according to standard EN 84 (1997). Specimens were covered with distilled water, the volume of which was five times the volume of the samples. Subsequently they were placed in the reactor and held under vacuum of 0.04 bar (abs) for 20 min. Afterwards, the blocks remained immersed for 2 h, and the water was substituted fresh one for the first time. The specimens remained immersed in the distilled water for 14 days, during which water was refreshed 10 times (including the first water change). The leached specimens were gently air dried in a constant climate, then oven dried at 103 ± 2°C for 96 h and finally were re-weighed to acquire their dry weight after leaching (m_L). Weight per cent change after leaching (WC_L) for each specimen was calculated using the following equation.

$$WC_L(\%) = 100 \times (m_L - m_0)/m_0. \quad (2)$$

In all tests, six replicates were used per variable, and the same series of untreated wood specimens were also used for comparison and for each parameter.

Termite resistance

Once treated, the specimens were placed in contact with termites following the methodology explained in the European standard EN 117 (2012).

Each wood specimen was in contact with a colony of termites according to the following methodology: Remoisten sand (1 volume of water to 4 volumes of sand) and small pieces of wood (approximately 0.5 g) were introduced and pushed down to the bottom of each container. Then, a colony of termites comprising 250 workers and a number of 2–3 soldiers and nymphs were introduced to each container. The test containers were incubated in a culturing chamber, with air-circulation controlled at 26 ± 2°C, at a minimum relative humidity of 70 ± 5%. Over a period of two or four days after setting up the colonies, in each recipient, a glass ring against one of the vertical walls of the container was introduced in the middle of this wall. Afterwards, a wood specimen

Table 2. Mean (and standard deviation in parentheses) of weight per cent changes related to the tested specimens.

	Concentration (%)	Ageing	Weight change, impregnation (%)	Weight change, after leaching (%)
Nano-ZnB	0.5	Leached	2.0 (0.47)	0.7 (0.64)
		Unleached	2.1 (0.51)	–
	1.0	Leached	4.3 (1.11)	2.9 (1.22)
		Unleached	4.4 (1.00)	–
	2.0	Leached	9.8 (2.42)	8.2 (2.38)
		Unleached	9.7 (2.34)	–
Nano-ZnO	0.5	Leached	2.1 (0.90)	0.8 (0.97)
		Unleached	2.3 (0.67)	–
	1.0	Leached	5.4 (1.37)	4.0 (1.51)
		Unleached	5.2 (1.22)	–
	2.0	Leached	10.1 (2.48)	8.6 (2.45)
		Unleached	10.7 (3.03)	–
Untreated		Leached	0.0 (0.00)	−1.5 (0.51)
		Unleached	0.0 (0.00)	–

in each container was placed. All the test containers were placed in the culturing chamber during a period of 8 weeks, during which the humidity of the sand in the recipients was controlled.

At the end of the test, the wood specimens were removed from each container for visual examination according to the following criteria: 0: no attack, 1: attempted attack (superficial erosion), 2: slight attack (erosion of 1 mm in depth and/or single tunnelling to a depth of up to 3 mm), 3: average attack (erosion of <1 mm in depth and/or isolated tunnelling of a depth >3 mm not enlarging to form cavities), and 4: strong attack (erosion of >1 mm to <3 mm in depth and/or tunnelling penetrating to a depth >3 mm and enlarging to form a cavity in the body of the test specimen).

In addition, the total number of termites still alive in each test container, the survival level of the workers, and the presence of living soldiers (or nymphs) were determined. Furthermore, the weight (mass) loss of each wood specimen was also determined, even though this is not a requirement of the European standard.

In order to detect statistically significant differences among the mean values acquired in this research, one-way analysis of variance ($\alpha = 0.05$) was carried out using SPSS 18.0. Microsoft Excel 2007 was used to determine the regression models and coefficient of determination values.

Results and discussion

The mean weight per cent changes (e.g. retention levels) after each treatment are shown in Table 2.

Regarding hygroscopicity, it was found that impregnation of wood specimens with nano-ZnB and nano-ZnO dispersions did not result in any significant moisture content change of the used specimens.

From Figure 1, it is obvious that weight changes (compared to the dry state) after impregnation and leaching of the specimens showed strong linear correlation ($R^2 > 0.99$) against the concentration of the used dispersions. This indicates that absolute leaching was higher at higher concentrations, a result that has also been reported by Clausen *et al.* (2011).

Table 3 shows the results concerning the survivals of termites as well as the weight loss values after the tests indicating that the survival rate of the termite workers was reduced from 58.0% (for leached specimens) and 63.1% (for unleached specimens) to 0% for all tested treatments. This proves a strong improvement in terms of termite workers mortality regardless of the dispersion concentration.

Regarding the inhibition of termite feeding, Figure 2 indicates that the related weight loss was strongly ($R^2 > 0.85$) correlated to the nominal concentration of the used dispersions and can be described by a power model. According to the one-way ANOVA (least square difference) results for the unleached nano-ZnB impregnated specimens, an increase of concentration from 0% to 0.5% did not result in a statistically significant reduction ($\alpha = 0.05$) of termite feeding, indicating that concentrations up to 0.5% are not sufficient for improving the termite durability of beech wood. On the contrary, impregnation of wood with nano-ZnB dispersions having concentrations of 1% and 2% resulted in a significant reduction of

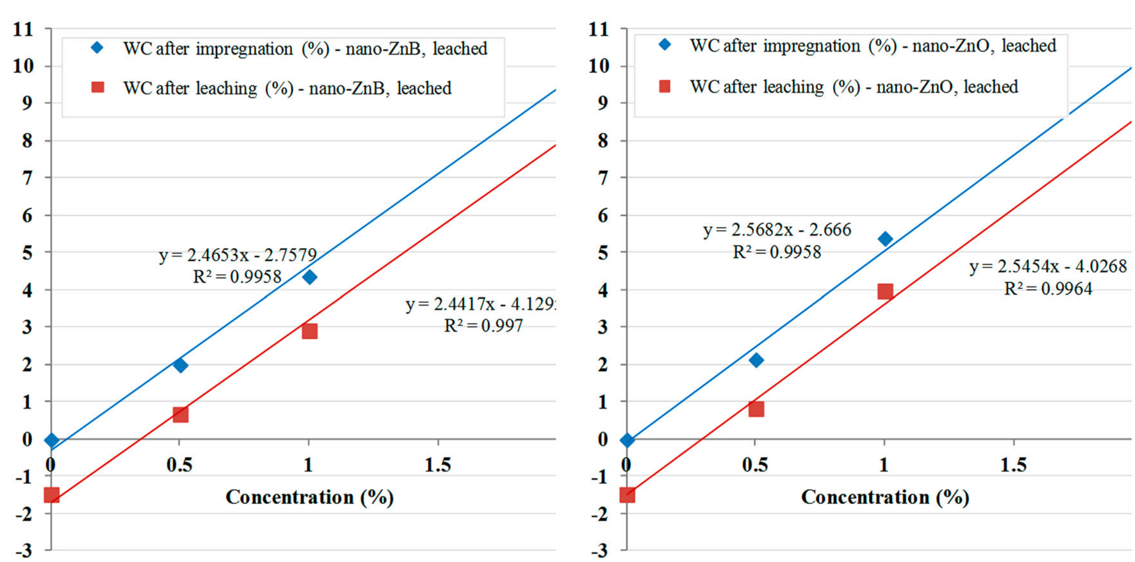

Figure 1. Mean values of dry weight per cent change due to impregnation and due to leaching for the tested range of dispersion concentrations.

Table 3. Mean (and standard deviation in parentheses) of attack degree, percentage of survivals and weight losses related to the tested specimens.

	Concentration (%)	Ageing	Attack degree	Survivals (%)	Weight loss (%)
Nano-ZnB	0.5	Leached	0	0.0 (0.0)	4.6 (1.2)
		Unleached	1	0.0 (0.0)	6.3 (2.5)
	1.0	Leached	0	0.0 (0.0)	3.4 (0.3)
		Unleached	1	0.0 (0.0)	3.6 (1.2)
	2.0	Leached	0	0.0 (0.0)	2.2 (0.3)
		Unleached	0	0.0 (0.0)	1.5 (0.7)
Nano-ZnO	0.5	Leached	1	0.0 (0.0)	2.5 (0.8)
		Unleached	1	0.0 (0.0)	2.5 (1.1)
	1.0	Leached	0	0.0 (0.0)	1.9 (0.3)
		Unleached	1	0.0 (0.0)	1.4 (0.4)
	2.0	Leached	0	0.0 (0.0)	1.7 (0.2)
		Unleached	0	0.0 (0.0)	1.3 (0.3)
Untreated		Leached	4	58.0 (18.3)	9.6 (2.0)
		Unleached	3	63.1 (6.0)	8.0 (2.2)

weight loss. Increase of nano-ZnB concentration from 1% to 2% also induced significant increase of beech wood durability against termites.

Regarding nano-ZnO treated specimens, the use of all tested dispersions resulted in a rather significant improvement of biological durability compared to the durability of untreated specimens. Furthermore, the increase of nano-ZnO concentration from 0.5% to 1% and 2% did not induce additional improvement of durability for the tested specimens. From the above findings, it can be concluded that nano-ZnO dispersions with concentration of 0.5% are adequate to significantly improve the termite durability of European beech wood because further increase of the concentration did not induce additional improvement of durability. It is also evident that nano-ZnO dispersions seem more efficient than nano-ZnB in terms of concentration because they induce significant termite durability improvement at concentrations as low as 0.5% while nano-ZnB should be used at concentrations higher than 1% in order to induce similar changes.

Regarding the effects of water leaching on the untreated specimens, there was no significant difference shown in terms of termite feeding among leached and non-leached untreated specimens, indicating that the water soluble substances of European beech wood do not seem to have a significant effect on termite durability of beech wood.

For the treated specimens, water leaching marginally increased termite feeding for both used dispersions and all concentrations. Nevertheless, this increase was not statistically significant for all cases. The above findings, along with those related to weight per cent changes (Figure 1), lead to the conclusion that for both tested dispersions and for all tested concentrations, water leaching did not induce significant increase of termite feeding. The above conclusions are in agreement with related results reported by others (Clausen *et al.* 2010b).

Conclusions

In this work, the resistance of European beech (*F. sylvatica* L.) wood impregnated with nano-ZnO and nano-ZnB against the termite *R. grassei* Clement was investigated. Three different concentrations (0.5%, 1%, 2%) of the nanocompounds were tested and the effects of water leaching were also investigated.

The survival rate of the termite workers was severely reduced by all tested treatments, proving a strong improvement in terms of termite workers mortality disregarding the concentration of the used dispersion.

Nano-ZnO dispersions with concentration of 0.5% were adequate in order to significantly improve the termite durability of European beech wood, but further increase of the concentration was not connected to an additional corresponding improvement.

Nano-ZnO dispersions seemed more efficient than nano-ZnB in terms of concentration because they induced

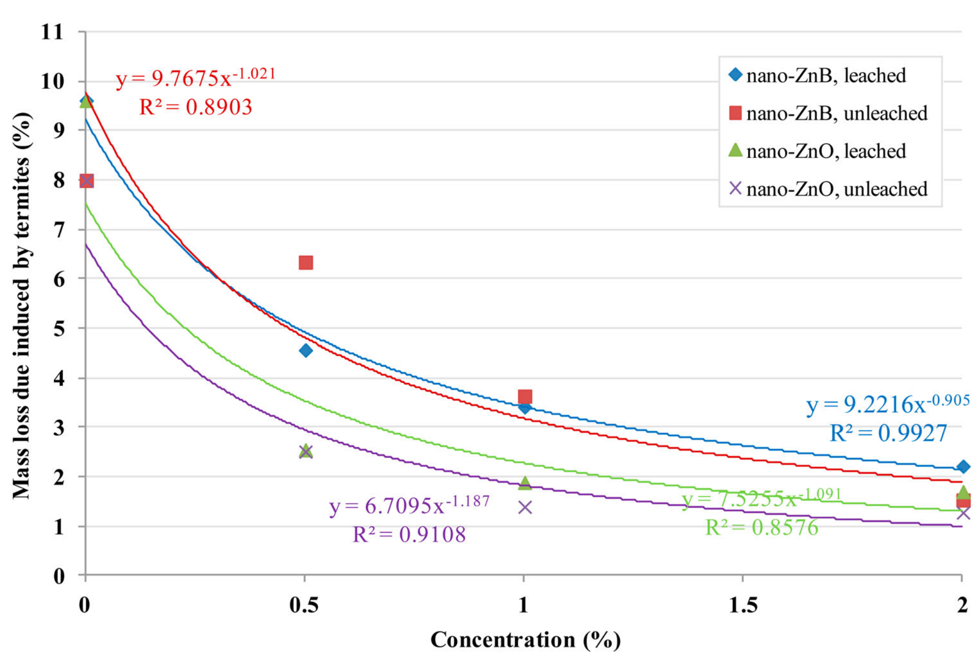

Figure 2. Mean weight loss induced by termite feeding for the tested range of dispersion concentrations.

significant termite durability improvement at concentrations as low as 0.5%; on the other hand, nano-ZnB had to be used at concentrations at least 1% in order to induce similar changes. For both dispersions and for all tested concentrations, water leaching did not induce any significant increase of termite feeding.

The results of this study can be characterised as promising, but in order to get closer to real-time applications, more in-depth research needs to be carried out considering the effects of nano-particle properties (e.g. size distribution, shape) against the performance of wood products for outdoor applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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