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The termite resistance of wood impregnated with nano-zinc oxide and nano-zinc borate dispersions

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ABSTRACT

In this work, the effects of the impregnation with nano-ZnO and nano-ZnB dispersions on the termite resistance of European beech wood were investigated. Three different concentrations (namely 0.5%, 1% and 2%) of the above two materials were tested. Water leaching effect was also investigated. It was concluded that a severe effect in terms of termite workers mortality is induced by the use of both dispersions even at the lowest concentration. In terms of termite feeding, Nano-ZnO dispersions seem more efficient than nano-ZnB because they induce significant improvement at concentrations as low as 0.5% while nano-ZnB should be used at concentrations at least 1% in order to induce similar changes. Nano-ZnB dispersions are efficient in terms of termite resistance for concentrations at least 1%. Further increasing concentration to 2% resulted to a respective increase of termite durability. For both tested dispersions and for all tested concentrations water leaching did not induce significant increase of termite feeding.

Keywords: nano zinc oxide, nano zinc borate, impregnation, termite resistance, wood protection

1. INTRODUCTION

The introduction of nanotechnology in the field of wood technology has opened a door to a wide range of possible applications. Among the most important of these is the use of nano-sized metals in the improvement of technical properties of wood. Nano-sized metals are very effective in wood protection applications mainly because, due to their size, they increase the effective surface area of the metal in an evenly dispersed layer (Freeman and McIntyre 2008) but also because such particles can penetrate through wood cell wall openings and provide the potential for high retention therefore resulting to higher durability of wood (Kartal *et al.* 2009).

Nano-zinc oxide (nano-ZnO) and nano zinc borate (nano-ZnB) are two well-known examples of nano-sized metals used for the enforcement of some properties of organic materials. Nano-ZnO has been widely used used as wood coating additive for the improvement of its UV stability and biological resistance (Hegedus *et al.* 2008, Yu *et al.* 2010, Weilhelt *et al.* 2010, Lei *et al.* 2010, Lowry *et al.* 2008, AWPA 2010, Auclair *et al.* 2011, Saha *et al.* 2011). Nano-ZnB has been used as an effective compound for improving fire retardancy (Garba 1999) as well as antifungal and anti-insect properties of wood (Manning and Laks 1998).

Until recently, there was not so much information about the use of nano-ZnO and nano-ZnB as additives in impregnation solutions but during the last years work has been conducted in terms of using nano-ZnO as additive in impregnation solutions in order to increase retention extend the service life to wood. (Kartal *et al.* 2009, Clausen *et al.* 2010, Lykidis *et al.* 2013, Akhtari *et al.* 2013). Some authors (Clausen *et al.* 2010b) reported that nano-ZnO-treated wood inhibited some decay fungi, except those that are zinc-tolerant (e.g. *Postia placenta*). They also reported that nano-ZnO inhibited termite feeding and caused moderate termite mortality and inhibition. The same authors (Clausen *et al.* 2010) reported almost no leaching in nano-ZnO impregnated pine wood specimens after a laboratory test. They also informed that, after 12 months of outdoor exposure, significant UV protection was achieved while for specimens treated with high concentrations of nano-ZnO high chemical depletion was shown. Furthermore, nano-ZnO concentration higher than 2.5% provided substantial resistance to water absorption following 12 months of outdoor exposure compared to untreated and unweathered pine wood. Clausen *et al.* (2011) have reported high leaching and termite resistance of pine wood impregnated with nano-ZnO at concentrations up to 5%. Both leachability and termite resistance were and not influenced by the nano-ZnO particle dimensions. Mass loss of wood by eastern subterranean termites was less than 4% and mortality was greater than 94% for the tested specimens. Nemeth *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) investigated the spectra of wood specimens impregnated with nano-ZnO concluding that there were not present significant changes in lignin and carbohydrates after exposure to *Trametes versicolor* indicating fungicide effects of the ZnO nanoparticles on this species. Lykidis *et al.* (2013) investigated the brown rot resistance of black pine (*Pinus nigra* L.) wood, pressure-treated in an autoclave with nano-ZnO and nano-ZnB dispersions. Mean weight losses for *P. nigra* sapwood exposed to *Coniophora puteana* were 0.6% when treated with nano-ZnB. On the contrary, the impregnation of pine wood with nano-ZnO resulted in less durability (weight loss of 35.9%) against the same fungi. Farahani and Banikarim (2013) investigated the decay resistance of wood- polypropylene composites (WPCs) treated with nano-ZnO against the white rot fungus *Trametes versicolor* and the brown rot fungus *Coniophora puteana* and concluded that nano-ZnO improved the decay resistance of the composite against the fungi.

In this work the effects of impregnation with nano-ZnO and nano-ZnB dispersions of three different concentrations on the termite resistance of beech wood were investigated.

2. EXPERIMENTAL METHODS

2.1 Preparation of samples

For the purposes of this work wood specimens with dimensions of 25x25x15 mm, free of defects were prepared from mature sapwood of European beech (*Fagus sylvatica* L.) wood were prepared. All specimens were initially dried in a ventilated oven at 103±2°C for 96h and then weighed to acquire their dry weight prior to impregnation (m_0). Afterwards they were conditioned prior to the impregnations at 20°C and 65% relative humidity (RH) using a desiccator loaded with saturated $NaNO_2$ solution for approximately one month until constant weight. The moisture content of the conditioned specimens varied between 9.5% and 9.8%.

2.2 Impregnation and leaching

For the impregnation of the wood specimens, two types of dispersions were used, namely nano-ZnB and nano-ZnO. The nano-dispersions were provided by NanoPhos SA (Lavrio, Greece). The physical and chemical properties of the above materials have been previously reported

(Lykidis *et al.* 2013). The impregnations were 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 15s, while vigorously stirred. The loaded reactor was then pressurized at 6.0±0.1 bar for 60 min. Finally, the dispersion was withdrawn and the specimens were vacuum-treated at 0.56±0.01 bar for 15min. 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 as above at 103±2°C for 96h and were re- weighed in order to get their dry weight after impregnation (m_i). Weight percent change after impregnation (WC_i) for each specimen was calculated using Eq. 1.

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

Leaching was carried out according to EN84. Samples 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 were held under vacuum of 0.04 bar (abs) for 20 min. Afterwards, the samples stayed immersed for 2 h and the water was substituted fresh one for the first time. The specimens stayed immersed in the distilled water for 14 days during which water was refreshed ten times (including the first water change). The leached specimens were gently air dried in a constant climate, oven dried as above at 103±2°C for 96h and were finally re- weighed to acquire their dry weight after leaching (m_L). Weight percent change after leaching (WC_L) for each specimen was calculated using Eq. 2.

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

A series of untreated specimens were also used for comparison and for each parameter six replicates were used. All the parameters employed are presented in Table 1.

Table 1: Treatments used in this research

No	Impregnation material	Concentration [%]	Leaching	Samples
1	Untreated	-	Yes	6
2	Untreated	-	No	6
3	nano-ZnB	2.0%	Yes	6
4	nano-ZnB	2.0%	No	6
5	nano-ZnB	1.0%	Yes	6
6	nano-ZnB	1.0%	No	6
7	nano-ZnB	0.5%	Yes	6
8	nano-ZnB	0.5%	No	6
9	nano-ZnO	2.0%	Yes	6
10	nano-ZnO	2.0%	No	6
11	nano-ZnO	1.0%	Yes	6
12	nano-ZnO	1.0%	No	6
13	nano-ZnO	0.5%	Yes	6
14	nano-ZnO	0.5%	No	6

2.3 Termite resistance

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

The species of termite used has been *Reticulitermes grassei* (Clement), cultured in the culturing chamber under controlled conditions at 28ºC and 80 % of relative humidity.

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 the each container. Then, a colony composed by 250 workers, and a number of 2-3 soldiers and nymphs were also introduced to each container. The test containers were incubated in a culturing chamber, with air circulation, controlled at (26 ±2) °C and 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 and in the middle of this wall was introduced. Afterwards, a wood specimen in each container was also 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 tunneling to a depth of up to 3 mm), 3: average attack (erosion of < 1 mm in depth and/or isolated tunneling 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 tunneling 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 living in each test container, the survival level of the workers, as well as the presence of living soldiers and/or nymphs was determined. Furthermore, although it is not a requirement of the Standard, the weight loss of each specimen was also determined.

3. RESULTS AND DISCUSSION

All acquired results by this research are presented in Table 2. Regarding hygroscopicity, it was found that the impregnation of specimens with nano-ZnB and nano-ZnO dispersions did not result to significant moisture content changes of the used specimens.

From Fig.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 fact that has also been reported by Clausen *et al.* (2011).

From Table 2 it is evident 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, proving a strong improvement in terms of termite workers mortality disregarding the concentration of the used dispersion.

In terms of Fig. 2 it seems that weight loss induced by termite feeding is strongly (R^2>0.85) correlated to the nominal concentration of the used dispersions and can be described by a power model.

Table 2: Results of moisture contents, weight percent changes, weight losses and termite survival rates related to the tested specimens

	nano-ZnB						nano-ZnO						untreated	
	0.5%		1.0%		2.0%		0.5%		1.0%		2.0%			
	leached	unleached	leached	unleached	leached	unleached	leached	unleached	leached	unleached	leached	unleached	leached	unleached
Weight change, impregnation [%]	2.0[1]	2.1	4.3	4.4	9.8	9.7	2.1	2.3	5.4	5.2	10.1	10.7	0.0	0.0
	0.47[2]	0.51	1.11	1.00	2.42	2.34	0.90	0.67	1.37	1.22	2.48	3.03	0.00	0.00
Weight change, leaching [%]	0.7	.	2.9	.	8.2	.	0.8	.	4.0	.	8.6	.	-1.5	.
	0.64	.	1.22	.	2.38	.	0.97	.	1.51	.	2.45	.	0.51	.
Weight loss, termite feeding [%]	4.6	6.3	3.4	3.6	2.2	1.5	2.5	2.5	1.9	1.4	1.7	1.3	9.6	8.0
	1.2	2.5	0.3	1.2	0.3	0.7	0.8	1.1	0.3	0.4	0.2	0.3	2.0	2.2
Survival of workers [%]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	58.0	63.1
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18.3	6.0

[1]: Mean
[2]: Standard deviation

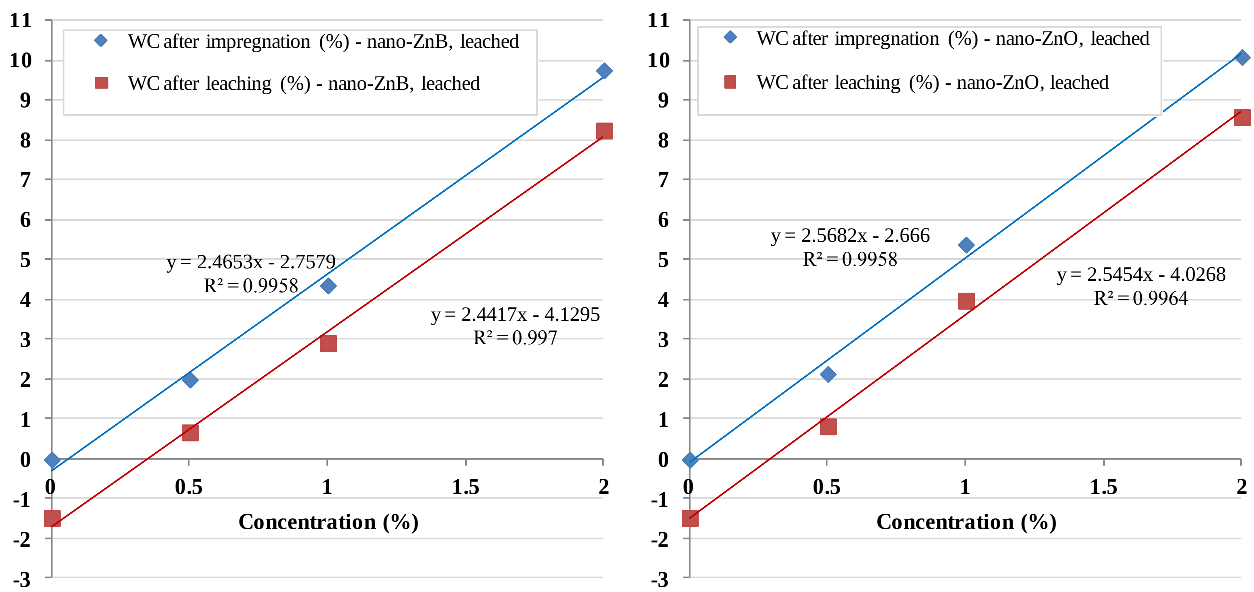

Figure 1: Mean values of dry weight percent change due to impregnation and due to leaching for the tested dispersion concentrations

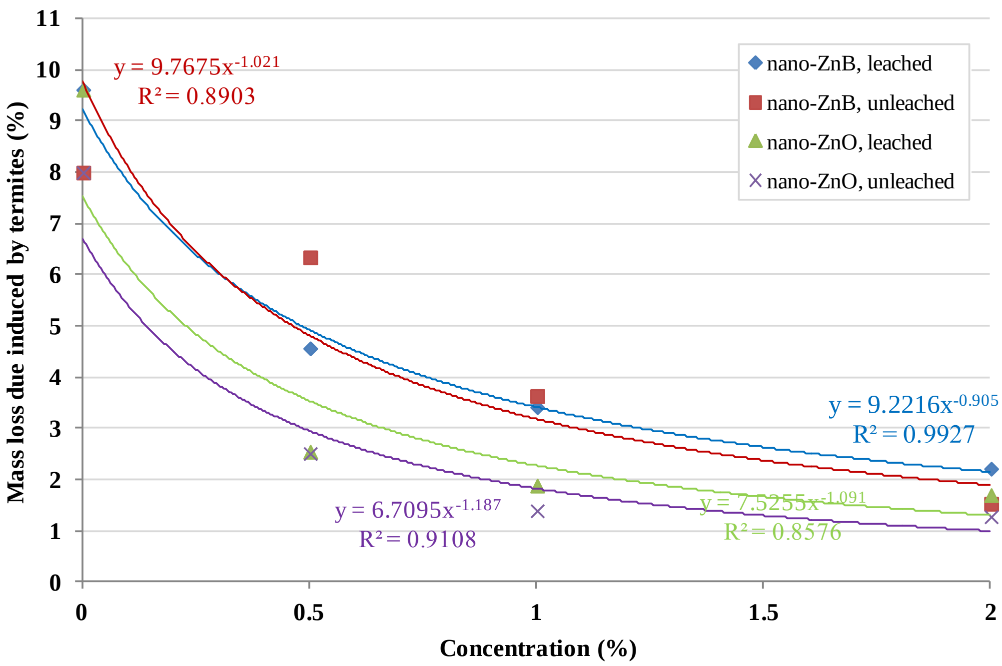

Figure 2: Mean weight loss induced by termite feeding for the tested dispersion concentrations

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 to a statistically significant reduction ($\alpha=0.05$) of termite feeding indicating that concentrations up to 0.5% are not sufficient for the improvement of termite durability of European beech wood. On the contrary, impregnation with nano-ZnB dispersions with concentrations of 1 and 2% resulted to a significant reduction of weight loss. Increase of the 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 to a significant improvement of termite 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 termite durability for the tested specimens. From the above findings it can be concluded that nano-ZnO dispersions with concentration of 0.5% are adequate in order to significantly improve the termite durability of European beech wood but further increase of the concentration is not related to an additional corresponding improvement. 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 at least 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 percent changes (Fig. 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*. 2010).

4. CONCLUSIONS

The main conclusions that can be drawn from the results of this work are summarized below:

- 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% are adequate in order to significantly improve the termite durability of European beech wood but further increase of the concentration is not related to an additional corresponding improvement.

- 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 at least 1% in order to induce similar changes.

- For both tested dispersions and for all tested concentrations water leaching did not induce significant increase of termite feeding.

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