



Termite resistance of pine wood treated with nano metal fluorides

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Abstract

Fluorides are well-known as wood preservatives. One of the limitations of fluoride-based wood preservatives is their high leachability. Alternative to current fluoride salts such as NaF used in wood protection are low water-soluble fluorides. However, impregnation of low water-soluble fluorides into wood poses a challenge. To address this challenge, low water-soluble fluorides like calcium fluoride (CaF₂) and magnesium fluoride (MgF₂) were synthesized as nanoparticles via the fluorolytic sol–gel synthesis and then impregnated into wood specimens. In this study, the toxicity of nano metal fluorides was assessed by termite mortality, mass loss and visual analysis of treated specimens after eight weeks of exposure to termites, *Coptotermes formosanus*. Nano metal fluorides with sol concentrations of 0.5 M and higher were found to be effective against termites resulting in 100% termite mortality and significantly inhibited termite feeding. Among the formulations tested, the least damage was found for specimens treated with combinations of CaF₂ and MgF₂ with an average mass loss less than 1% and visual rating of “1”. These results demonstrate the efficacy of low water-soluble nano metal fluorides to protect wood from termite attack.

1 Introduction

Termites cause significant structural damage to timber resulting in high economic losses (Pimentel et al. 2005). The invasive Formosan subterranean termite species *Coptotermes formosanus*, originating from China and Taiwan, has been successful in spreading to southern parts of the United States such as Florida (Chouvenc et al. 2016). Globally, the estimated economic costs from damage to goods and services due to *C. formosanus* was found to be > US\$30.2 billion per year (Bradshaw et al. 2016). These costs are predicted to rise as the population of *C. formosanus* is expected to increase by 15–20%, with the warming of the environment due to climate change (Buczowski and Bertelsmeier 2017). Thus, there are ongoing research efforts to find effective wood preservatives and wood modification technologies to control the consequent damage to timber products from the spread of *C. formosanus*.

Wood modification techniques such as acetylation and furfurylation have been evaluated for their resistance to termites. Acetylated radiata pine (both leached and unleached) in EN 117 tests was found to be durable against *Reticulitermes banyulensis* resulting in mass loss lower than 3% (Gascón-Garrido et al. 2013). However, acetylated wood was not durable against *C. formosanus* in a forced feeding test as even 20% acetylated larch resulted in a mass loss of 4.2% (Imamura and Nishimoto 1986). Besides wood modification treatments, current termiticides available on the market contain active ingredients such as bifenthrin, cypermethrin, fipronil, and permethrin (Xie et al. 2013). Although effective, some of these ingredients may be toxic to human health and environment. Fipronil poisoning was reported to cause seizures, while permethrin was found to be toxic to aquatic organisms (Weston et al. 2005; Dhang 2011). An alternative to commercial termiticides are nanoparticles as their smaller size allows for improved penetration into wood (Evans et al. 2008; Taghiyari 2015). Recently, several studies have reported on the efficacy provided by the reduction in size of commercial biocidal actives like copper, boron or zinc (Clausen et al. 2011; Civardi et al. 2015; Ibáñez et al. 2019). In the form of nanoparticles, they were tested for their efficacy against termites (Kartal et al. 2009; Mantanis et al. 2014; Terzi et al. 2016; Lykidis et al. 2018). In a four week no-choice test, unleached southern yellow pine wood treated

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with nanoboron had lower mass loss than those treated with nanocopper and nanozinc (Kartal et al. 2009). In addition, unleached nanoboron-treated specimens resulted in 100% termite mortality (Kartal et al. 2009). Another study tested black pine wood treated with nano formulations of zinc oxide, zinc borate and copper oxide against *C. formosanus* (Mantanis et al. 2014). In this three week no-choice test, nanozinc borate treated wood had mass loss lower than specimens treated with nanozinc and nanocopper (Mantanis et al. 2014). Another wood preservative that could be studied for their biocidal efficacy in the form of nanoparticles are fluorides. There are several studies on the efficacy of NaF, but no study has reported on termite resistance using nano metal fluorides.

One of the advantages of fluoride in wood preservatives is that they are effective in low concentrations (Freitag and Morrell 2005). A study on dry wood and subterranean termites found that NaF was more effective compared to disodium octaborate tetrahydrate (DOT) as it led to lower weight losses (Kartal et al. 2019). Concentration of 1% NaF in particleboard (unleached) resulted in a mass loss of 2.3% after three weeks of exposure against *C. formosanus* (Tascioglu et al. 2017). However, the termite resistance was lost when the NaF-treated particleboard was leached. Another study reported on field efficacy of NaF treatment against the subterranean termites *Reticulitermes flaviceps* (Pan et al. 2015). A choice test done with 0.057% (w/w) NaF-treated wood inhibited attack from *R. flaviceps* (Pan et al. 2015). The research also reported that a concentration of 0.1% (w/w) would protect timber from wood-degrading organisms. However, a follow-up study by the same research group concluded that more than 90% of fluoride from the NaF-treated blocks was leached into the surrounding soil (Pan and Wang 2015). Thus, the studies show that there is evidence of the efficacy of fluoride against termites, however, there is a need to improve its resistance against leaching.

The high leaching susceptibility of NaF is expected because of its high water solubility of 40 g/L (Roark 1926). Therefore, in the past, fluoride was combined with co-biocides to reduce its leaching and increase the biocide efficacy. Mixture of fluorine-chromium-arsenic was found to be toxic to three termite species, *Nasutitermes exitosus*, *Coptotermes acinaciformis*, and *Coptotermes lacteus* (Gay and Schulz 1965). However, awareness of environmental and health risks associated with chromium (Cr) and arsenic (As) has led to their restricted application in wood preservation. Without these co-biocides it becomes challenging to use approved fluoride compounds in wood protection products for outdoor application. This is one of the reasons for the decline in use of fluoride compounds in wood preservation. A potential way to overcome this challenge of high leachability is to test metal fluorides (MF₂) with low water solubility such as calcium fluoride (CaF₂) and magnesium fluoride (MgF₂),

but it is difficult to impregnate wood with crystalline low water-soluble fluorides. A way to overcome this limitation is to synthesize low water-soluble fluorides in the form of nanoparticles.

Nano metal fluorides are increasingly accessible since the fluorolytic sol gel synthesis was reported in 2003 (Kemnitz et al. 2003). Based on this synthetic accessibility, nano metal fluorides have been applied to anti-reflective coatings, bio-medicine and bio-plastics (Sun and Chow 2008; Krahl et al. 2016; Mahn and Kemnitz 2019). The homodispersed nanoparticles have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and dynamic light scattering (DLS) (Usmani et al. 2018). The mean particle size distribution of these nanoparticles was below 25 nm. It was shown that wood can be successfully impregnated with these nano metal fluoride particles. The distribution of these nano metal fluorides in cross-cut sections of treated wood was confirmed with scanning electron microscopy (Usmani et al. 2018). The average retention of MgF₂ and CaF₂ in wood specimens was 5 and 6%, respectively (Usmani et al. 2018). More importantly, it was found that wood treated with nano metal fluorides had average mass loss of only 2% when attacked by brown-rot fungi, *Coniophora puteana*. Thus, it was shown that nanoscopic homodispersed MgF₂ and CaF₂ synthesized via the fluorolytic sol-gel synthesis can be successfully used for timber treatment against *C. puteana* (Usmani et al. 2018). Consequently, the following study reports on biocide efficacy of nano metal fluorides against termites, *Coptotermes formosanus*. Here, two different formulations of CaF₂ were evaluated, one in ethylene glycol and another one in lactic acid. In addition to ethylene glycol, lactic acid as a solvent was tested as it is known to be biodegradable and compostable (Garlotta 2001). Thus, in the present study, low water-soluble fluorides MgF₂ and CaF₂ synthesized as nanoparticles were investigated for their efficacy against the subterranean termites, *C. formosanus*.

2 Materials and methods

2.1 Test chemicals

Sols of CaF₂ and MgF₂ were synthesized using calcium oxide, calcium lactate and magnesium ethoxide as precursors, followed by fluorination with HF as reported earlier (Usmani et al. 2018). The sols were synthesized with ethylene glycol as solvent. A combination of CaF₂ and MgF₂ was also synthesized in ethylene glycol. In addition, another formulation of CaF₂ sol was synthesized in lactic acid (Mahn and Kemnitz 2019). A 0.1 M NaF solution was also prepared for impregnation into wood specimens for comparison.

2.2 Treatment

Wood samples of dimensions 15 mm x 25 mm x 50 mm (radial x tangential x longitudinal) were prepared from Scots pine sapwood (*Pinus sylvestris*). Sols of MgF₂ and CaF₂ were diluted with ethanol to prepare the solutions at their respective concentration for impregnation of wood. For better penetration of the solutions into the wood, the samples were oven-dried and evacuated at 0.1–0.4 kPa for 1 h prior to impregnation. After 1 h, the solutions were introduced into the vacuum chamber and then the specimens were soaked in it for 2 h at ambient pressure and 20–23 °C. After impregnation, the specimens were weighed and conditioned for 4 weeks at 20–23 °C and 65% relative humidity to achieve moisture equilibrium.

2.3 Termite resistance test

The tests against termite species, *C. formosanus* were performed in accordance with EN 117 (2012). The number of termites for each experimental setup was 250 workers and 30 soldiers. After 8 weeks, the test specimens were removed and termite mortality was determined. The specimens were dried at 103 °C for 18 h and then weighed to record their final mass. These specimens were also visually examined and rated according to the assessment scheme for classifying termite attack according to EN 117. Based on the visual assessment and according to EN 350 (2016), the treated specimens were assigned to durability classes (“Durable” if the visual rating was 0 or 1, “Moderately Durable” if less than 50% test specimens had a visual rating of 3 or 4, and “Not Durable” if more than 50% had a visual rating of 3 or 4).

3 Results and discussion

The following results are separated into two sections based on the solvents used for synthesis of the respective sols. MgF₂ sol was synthesized with ethylene glycol as solvent. Two sols of CaF₂ were synthesized, one in ethylene glycol and another one in lactic acid. Combinations of MgF₂ and CaF₂ were also tested for efficacy in different formulations. The first formulation was the combination of MgF₂ and CaF₂ synthesized as a single sol in ethylene glycol. The second was the combination of separately synthesized sols of MgF₂ in ethylene glycol and CaF₂ in lactic acid. For comparison, NaF in H₂O as solvent was also tested.

Figure 1(a) and (b) present average termite mortality caused by respective treatment of test specimens. Termite mortality in control specimens in both series (Fig. 1a, b) was less than 50%, which is important for the overall validity of the EN 117 test. Additionally, termite mortality was significantly higher for almost all treated specimens compared to control specimens (p value < 0.01), except for specimens treated with 0.1 M CaF₂ which had a p value of 0.02 compared to control specimens.

In Fig. 1a, the termite mortality due to MgF₂-treated specimens was similar for concentrations below 0.5 M but did not reach 100%. Higher concentrations of 0.5 and 0.8 M MgF₂ resulted in 100% termite mortality. Termite mortalities caused by CaF₂ treatment in concentrations ranging from 0.1 to 0.4 M were similar. Again, termite mortality was lowest at 0.1 M CaF₂, while with higher concentrations of 0.2 and 0.4 M, the termite mortalities increased but did not reach 100%. A higher concentration of 0.8 M of CaF₂ was assumed to be more effective than a lower concentration of 0.5 M CaF₂, because the solubility

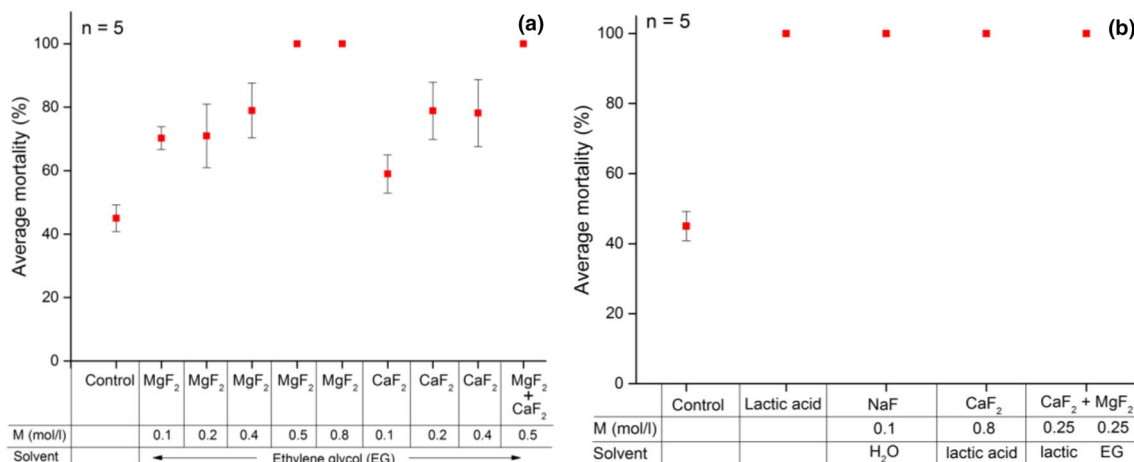


Fig. 1 Termite mortality due to treated specimens **a** nano metal fluorides synthesized with only ethylene glycol (EG) as solvent and **b** NaF and nano metal fluorides synthesized using lactic acid and ethylene glycol as solvent

of CaF_2 is lower than that of MgF_2 . Hence, CaF_2 at 0.5 M was not tested for efficacy against termites. Nonetheless, wood specimens treated with the single sol combination of MgF_2 and CaF_2 at 0.5 M caused 100% termite mortality. Treatment with NaF at 0.1 M also resulted in 100% mortality (Fig. 1b). Both, CaF_2 in lactic acid at 0.8 M and the combination of CaF_2 and MgF_2 at 0.5 M led to 100% termite mortality as well. The 100% termite mortality caused by nano metal fluorides at higher concentrations indicates that the toxicity of nano metal fluorides is the same as that of NaF and can be compared to nanoboron and nanozinc borate which also led to 100% termite mortality (Kartal et al. 2009; Mantanis et al. 2014; Tascioglu et al. 2017).

Surprisingly, the specimens treated only with lactic acid also resulted in 100% termite mortality (Fig. 1b). This suggests that lactic acid might provide resistance similar to that observed for acetylated radiata pine wood exposed to *R. banyulensis*, which also showed 100% termite mortality (Gascón-Garrido et al. 2013).

From Fig. 2a, it can be seen that the control specimens had significantly higher average mass loss due to termite attack than treated specimens (p value < 0.01). For MgF_2 and CaF_2 treated specimens respectively, mass loss was not affected by treatment concentration. However, MgF_2 treated specimens had lower average mass loss compared to CaF_2 treated specimens. The combination treatment of MgF_2 and CaF_2 (0.5 M) had a lower mass loss than CaF_2 treatment alone, but a similar average mass loss when compared to the MgF_2 treatments at higher concentration of 0.5 and 0.8 M. Therefore, the lower concentration of 0.5 M seems to be sufficient to promote antifeedant effect against *C. formosanus* similar to that observed for nanozinc borate (Mantanis et al. 2014).

From Fig. 2b, it is observed that the control specimens had significantly higher average mass loss compared to fluoride treated specimens (p value < 0.01). Average mass loss in lactic acid treated specimens was not significantly different compared to control specimens (p value = 0.70), suggesting that termites consumed lactic acid treated specimens as they consumed control specimens. NaF-treated wood had mass loss less than 2%. Mass loss was even lower for CaF_2 (in lactic acid) treatment alone and for the combination treatment of CaF_2 (in lactic) and MgF_2 (in ethylene glycol), respectively. This is somehow surprising since the freely available fluoride concentration in both, MgF_2 and CaF_2 , due to their lower solubility is significantly lower than in the case of NaF, although the nominal concentration of the latter is lower.

Figure 3 a shows the control specimens had higher visual ratings for damage than wood specimens treated with nano metal fluorides, which corresponds well with losses of mass (Fig. 2a). For both MgF_2 and CaF_2 treated specimens in the concentration from 0.1 to 0.4 M, the average visual assessment was above rating “3”. Based on this and according to EN 350 (2016), treated samples would be considered as “not durable”. For specimens treated with higher concentrations of MgF_2 (0.5 and 0.8 M), the visual ratings were below “2”. Similarly, test specimens treated with the single sol combination of MgF_2 and CaF_2 showed only minor damage with the average visual rating below “2”.

From Fig. 3b, it is observed that all the control specimens had an average visual rating of “4”, which was higher than those observed for treated specimens. Specimens treated with only lactic acid had an average visual rating of “2.5”, while NaF and CaF_2 (in lactic acid) treated specimens had average visual ratings below “2”. Therefore, fluoride treated specimens were less damaged than lactic acid treated

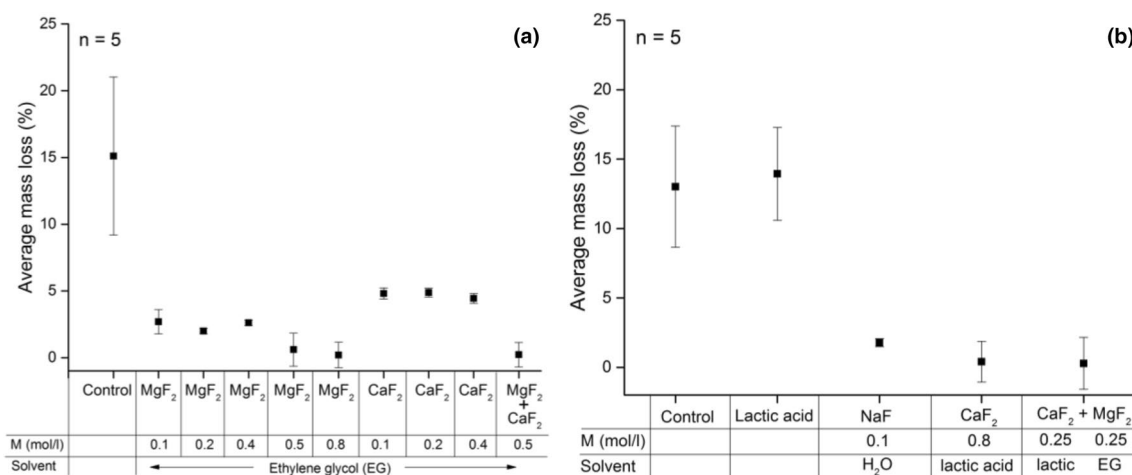


Fig. 2 Average mass loss of specimens **a** treated with nano metal fluorides synthesized with only ethylene glycol (EG) as solvent and **b** NaF and nano metal fluorides synthesized using lactic acid and ethylene glycol as solvent

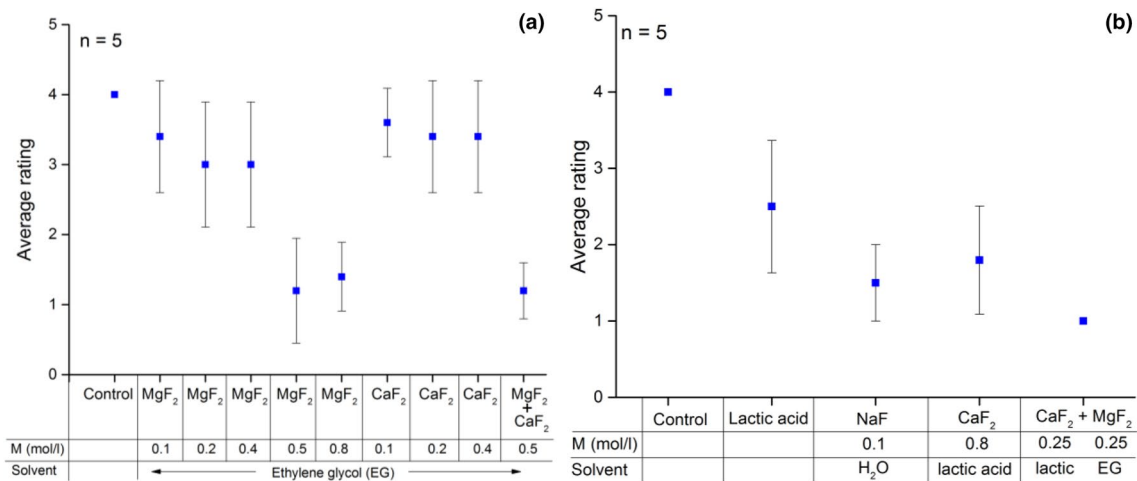


Fig. 3 Visual assessment rating **a** treated with NaF and nano metal fluorides synthesized using lactic acid and ethylene glycol (EG) as solvent, **b** nano metal fluorides synthesized with only ethylene glycol as solvent

specimens. Even though lactic acid treated specimens caused 100% termite mortality, they were more damaged compared to wood specimens treated with nano metal fluorides at concentrations of 0.5 and 0.8 M, which suggests that the effects of lactic acid had to accumulate over time with delayed mortality after the termites had consumed larger amounts of lactic acid treated wood. The delayed toxicity effect might be triggered by the low pH of lactic acid, which might be too acidic for the protists in the termite gut that are responsible for digesting the cellulose. However, these are unleached specimens and it is likely that lactic acid would be leached out under leaching conditions and thus reduce its toxic effect on the gut microorganisms. Finally, the two-step combination treatment of CaF₂ and MgF₂ led to even lower visual ratings of “1”, which would be considered “durable” according to durability classification in EN 350 (2016).

Nano metal fluoride treated specimens (MgF₂ and CaF₂) performed similar to NaF treated specimens. Wood specimens treated with NaF at 0.1 M had a lower rating for visual damage, lower mass loss, and higher termite mortality compared to control specimens. These results show that nano metal fluorides can be suitable alternatives to water soluble NaF. Evaluating the durability of nano-MgF₂ and -CaF₂ in comparison to NaF, at the first glance, it seems that higher concentrations of the nano-MF₂ systems are necessary. However, the opposite is true. The solubility of NaF is 40 g/L, while that of MgF₂ (130 mg/L) and of CaF₂ (16 mg/L) is significantly lower (Lide 2003). That means although nominally higher concentrations of MgF₂ and CaF₂ are needed for resistance against *C. formosanus*, just a very small part of the nanoparticles becomes dissolved, consequently a very low concentration of free fluoride ions is available. Thus, the latter fluorides are evidently more sustainable since the fluoride anions are released over a significantly larger time

scale as they are mainly present as insoluble MF₂ and only a small part is dissolved in wood specimens depending on moisture conditions.

Even the fact that MgF₂-treated specimens performed better than CaF₂ with lower average mass loss and lower visual ratings after termite attack by *C. formosanus* is due to the differences in their solubility. With 130 mg/L solubility of MgF₂ in water compared to just 16 mg/L solubility of CaF₂ in water, the same nominal concentration of both sols provides a free fluoride concentration in water being nearly higher by the factor of 10 for MgF₂. Surprisingly, the combination of CaF₂ and MgF₂ has similar effects at a lower concentration of 0.5 M than using either CaF₂ or MgF₂ alone at a higher concentration of 0.8 M. A reasonable explanation might be that not both metal fluorides exist as such in these combined systems but instead CaMgF₄ is formed, which has a solubility between that of CaF₂ and MgF₂ alone. Therefore, the combination provides an increased fluoride concentration compared with the single MgF₂ system. Although the formation of CaMgF₄ complexes has been reported previously, solubility data is not available for this complex compound (Krahl et al. 2016).

4 Conclusion

Previous research has reported that fluoride can be effective at low concentrations against fungi and termites (Gay and Schulz 1965; Freitag and Morrell 2005; Pan et al. 2015). This study shows that specimens treated with nano metal fluorides are less damaged than the severely attacked controls when exposed to termites. In this work, the low water-soluble nano metal fluorides CaF₂ and MgF₂ alone performed very well, but their combination performed even

better than NaF in visual ratings of treated wood specimens. This test was done over a duration of 8 weeks, while the termite resistance test with other nano treatments such as nanoboron and nano zinc borate reported in the literature were done for four weeks or less. Thus, it is expected that nano metal fluoride treated samples provide a longer-term protection compared to other nano formulations. Test specimens in this study were not leached prior to biological testing. In future experiments, leached wood specimens treated with nano metal fluorides have to be tested in comparison to leached NaF treated specimens. It can be assumed that susceptibility to leaching is significantly reduced with nano metal fluorides compared to NaF. The lower water solubility of MgF_2 and CaF_2 means that they can be used without fixatives making them more environmentally friendly and sustainable alternatives for wood protection against termites. The results from this study evidently show the potential of low water-soluble nano metal fluorides as effective and sustainable wood preservative formulations against termites.

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References

- Bradshaw CJA, Leroy B, Bellard C, Roiz D, Albert C, Fournier A, Barbet-Massin M, Salles JM, Simard F, Courchamp F (2016) Massive yet grossly underestimated global costs of invasive insects. *Nat Commun* 7:12986. <https://doi.org/10.1038/ncomms12986>
- Buczowski G, Bertelsmeier C (2017) Invasive termites in a changing climate: a global perspective. *Ecol Evol* 7:974–985. <https://doi.org/10.1002/ece3.2674>
- Chouvenc T, Li HF, Austin J et al (2016) Revisiting Coptotermes (Isoptera: Rhinotermitidae): a global taxonomic road map for species validity and distribution of an economically important subterranean termite genus. *Syst Entomol* 41:299–306. <https://doi.org/10.1111/syen.12157>
- Civardi C, Schubert M, Fey A, Wick P, Schwarze FW (2015) Micronized copper wood preservatives: efficacy of ion, nano, and bulk copper against the brown rot fungus *rhodonia placenta*. *PLoS One* 10(11):e0142578. <https://doi.org/10.1371/journal.pone.0142578>
- Clausen CA, Kartal SN, Arango RA, Green F (2011) The role of particle size of particulate nano-zinc oxide wood preservatives on termite mortality and leach resistance. *Nanoscale Res Lett* 6:1–5. <https://doi.org/10.1186/1556-276X-6-427>
- Dhang P (2011) Insecticides as Urban Pollutants. In: Dhang P (ed) *Urban pest management: an environmental perspective*. CABI, Cambridge, pp 1–18
- EN 117 (2012) Wood preservatives — Determination of toxic values against *Reticulitermes* species (European termites) (Laboratory method). European Committee for Standardization, Brussels
- EN 350 (2016) Durability of wood and wood-based products – Testing and classification of the durability to biological agents of wood and wood materials. European Committee for Standardization (CEN), Brussels
- Evans P, Matsunaga H, Kiguchi M (2008) Large-scale application of nanotechnology for wood protection. *Nat Nanotechnol* 3:577. <https://doi.org/10.1038/nnano.2008.286>
- Freitag C, Morrell JJ (2005) Development of threshold values for boron and fluoride in non-soil contact applications. *For Prod J* 55:97–101
- Garlotta D (2001) A literature review of poly(lactic acid). *J Polym Environ* 9:63–84. <https://doi.org/10.1023/A:1020200822435>
- Gascón-Garrido P, Oliver-Villanueva JV, Ibiza-Palacios MS, Militz H, Mai C, Adamopoulos S (2013) Resistance of wood modified with different technologies against Mediterranean termites (*Reticulitermes* spp.). *Int Biodeterior Biodegrad* 82:13–16. <https://doi.org/10.1016/j.ibiod.2012.07.024>
- Gay FJ, Schulz WO (1965) Comparison of two water-soluble wood preservatives against termite attack. *Holz Roh- Werkst* 23:6–9. <https://doi.org/10.1007/bf02619016>
- Ibáñez CM, Camargo A, Mantero C, Faccio R, Malanga A, Rabinovich M (2019) Effectiveness of micronizing zinc borate to improve its fungicidal properties. *BioResources* 14:6231–6246. <https://doi.org/10.15376/biores.14.3.6231-6246>
- Imamura Y, Nishimoto K (1986) Resistance of acetylated wood to attack by subterranean termites. *Wood Res* 72:37–44
- Kartal SN, Green F, Clausen CA (2009) Do the unique properties of nanometals affect leachability or efficacy against fungi and termites? *Int Biodeterior Biodegrad* 63:490–495. <https://doi.org/10.1016/j.ibiod.2009.01.007>
- Kartal SN, Terzi E, Yoshimura T (2019) Performance of fluoride and boron compounds against drywood and subterranean termites and decay and mold fungi. *J For Res*. <https://doi.org/10.1007/s11676-019-00939-4>
- Kemnitz E, Groß U, Rüdiger S, Shekar CS (2003) Amorphous metal fluorides with extraordinary high surface areas. *Angew Chemie Int Ed* 42(35):4251–4254. <https://doi.org/10.1002/anie.200351278>
- Krahl T, Broßke D, Scheurell K, Lintner B, Kemnitz E (2016) Novel aspects in the chemistry of the non-aqueous fluorolytic sol-gel synthesis of nanoscaled homodisperse MgF_2 sols for antireflective coatings. *J Mater Chem C* 4:1454–1466. <https://doi.org/10.1039/c5tc03764f>
- Lide DR (2003) *CRC Handbook of Chemistry and Physics*, 84th Edition, 2003–2004. *Handb Chem Phys*. <https://doi.org/10.1136/oem.53.7.504>
- Lykidis C, De Troya T, Conde M, Galván J, Mantanis G (2018) Termite resistance of beech wood treated with zinc oxide and zinc borate nanocompounds. *Wood Mater Sci Eng* 13(1):45–49. <https://doi.org/10.1080/17480272.2016.1257651>
- Mahn S, Kemnitz E (2019) Modification of low-molecular polylactic acid by CaF_2 nanoparticles: a new approach to change its material properties. *J Appl Polym Sci* 136:1–6. <https://doi.org/10.1002/app.47875>

- Mantanis G, Terzi E, Kartal SN, Papadopoulos AN (2014) Evaluation of mold, decay and termite resistance of pine wood treated with zinc- and copper-based nanocompounds. *Int Biodeterior Biodegrad* 90:140–144. <https://doi.org/10.1016/j.ibiod.2014.02.010>
- Pan C, Wang C (2015) Sodium fluoride for protection of wood against field populations of Subterranean Termites. *J Econ Entomol* 108:2121–2124. <https://doi.org/10.1093/jee/fov175>
- Pan C, Ruan G, Chen H, Zhang D (2015) Toxicity of sodium fluoride to subterranean termites and leachability as a wood preservative. *Eur J Wood Prod* 73:97–102. <https://doi.org/10.1007/s00107-014-0849-x>
- Pimentel D, Zuniga R, Morrison D (2005) Update on the environmental and economic costs associated with alien-invasive species in the United States. *Ecol Econ* 52:273–288. <https://doi.org/10.1016/j.ecolecon.2004.10.002>
- Roark RC (1926) Fluorides vs. fluosilicates as insecticides. *Science* 63:431–432
- Sun L, Chow LC (2008) Preparation and properties of nano-sized calcium fluoride for dental applications. *Dent Mater* 24:111–116. <https://doi.org/10.1016/j.dental.2007.03.003>
- Taghiyari HR (2015) Future prospects of wood preservation with nanotechnology. *Lignocellulose* 4:1–3
- Tascioglu C, Umemura K, Kusuma SS, Yoshimura T (2017) Potential utilization of sodium fluoride (NaF) as a biocide in particleboard production. *J Wood Sci* 63:652–657. <https://doi.org/10.1007/s10086-017-1654-z>
- Terzi E, Kartal SN, Yilgör N, Rautkari L, Yoshimura T (2016) Role of various nano-particles in prevention of fungal decay, mold growth and termite attack in wood, and their effect on weathering properties and water repellency. *Int Biodeterior Biodegrad* 107:77–87. <https://doi.org/10.1016/j.ibiod.2015.11.010>
- Usmani SM, Stephan I, Hübert T, Kemnitz E (2018) Nano metal fluorides for wood protection against fungi. *ACS Appl Nano Mater* 1(4):1444–1449. <https://doi.org/10.1021/acsanm.8b00144>
- Weston DP, Holmes RW, You J, Lydy MJ (2005) Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ Sci Technol* 39:9778–9784. <https://doi.org/10.1021/es0506354>
- Xie Y, Du Q, Huang Q, Lei C (2013) Evaluation of formic acid toxicity to subterranean termite, *Reticulitermes chinensis* Snyder. *Sociobiology* 60:453–458. <https://doi.org/10.13102/sociobiology.v60i4.453-458>

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