Mold and Larvae Resistance of Wood-Based Composites Incorporating Sodium Fluoride

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The efficacy of particleboards manufactured with sodium fluoride against mold fungi and *Hylotrupes bajulus* (L.) larvae was tested. Laboratory-size particleboards were manufactured from untreated wood particles with inclusion of fine sodium fluoride (NaF) at the 1, 1.5, and 3% levels relative to total particle weight. Sodium fluoride was introduced as powder during the manufacturing process just before blending resin with wood particles. The laboratory mold test indicated that even the lowest level of retention of NaF with or without leaching significantly reduced mold growth on particleboard surfaces when compared to the untreated control specimens. The increased retention of NaF from 1% to 3% further suppressed mold growth towards lowest levels even on leached specimens. The laboratory *Hylotrupes bajulus* larvae tests revealed that the particleboard environment with or without NaF is not appropriate for larvacidial activity. While the tested biocide, NaF, tested positive against mold growth on particleboard surfaces, no effect was determined relative to larval deaths.

Keywords: Particleboard; Sodium fluoride; Mold; Hylotrupes bajulus larvae

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INTRODUCTION

Wood-based composites have been increasingly used in indoor and outdoor construction applications worldwide for the last few decades since they represent the most economical way to replace the depleting solid wood supply. However, since such composites consist mostly of solid wood, they need to be properly protected when used in indoor or outdoor conditions where they are exposed to biological agents such as decay or mold fungi or wood-destroying insects.

Mold growth has been reported on several construction materials such as wood-based composites (OSB) (Laks *et al*. 2002), wood-polymer composites (Hosseinaei *et al*. 2012), agricultural fiber composites such as sugarcane bagasse particleboard (Garzon-Barrero *et al*. 2016), and agricultural fiber plastic composites (corn straw fiber/HDPE) (Xuan *et al*. 2017). They have been reported even on novel hybrid green composites produced from glass fibers and jute fabric skin with VARTM process (Terzi *et al*. 2018). Furthermore, mold growth indoors causes aesthetical and health problems such as asthma, and allergic rhinitis (Yang *et al*. 2007). It was reported that the mechanical strength of fiberboard exposed to mold and stain fungi was reduced about 50% while calculated mass loss was approximately between 12 to 18%. It was also mentioned that hemicellulose and α-cellulose were consumed by mold fungi, whereas lignin was hardy attacked (Chung *et al*. 1999).

The larvae of *Hylotrupes bajulus* (L.) (Old House Borer, House Longhorn) are structural insect pests of worldwide importance and bore through wood and feed on it. The resulted tunnels weaken structural integrity of timbers and wooden structures (Kacik *et al*. 2017). The name is somewhat misleading, since large number of infestations has been reported on buildings just between four to seven years old (Bora Care Technical Bulletin 2016).

Wood-based composites can be protected *via* two major treatment processes: 1) Post-treatment; a biocide is applied after the manufacturing process, or 2) In-process treatment; a biocide is applied during the manufacturing process. In general, the in-process treatment method has economic advantages since post-treatment requires modifications on manufacturing line, adding cost to the final product. An additional benefit of in-process treatment is the homogeneous distribution of biocide within the resulting product, which allows the end users to cut, drill, or notch the product any time (Gardner *et al*. 2003).

While chemical protection methods have been widely utilized in recent years, the application of chemical wood preservatives in living and working areas has been declining to reduce risks of toxicating indoor air. Therefore, chemical-free treatment methods or chemicals with environmentally green records have been evaluated, such as zinc borate (Tascioglu *et al*. 2014) or sodium fluoride. Sodium fluoride is also known as medication and primarily used to prevent tooth decay and osteoporosis in humans (O'Neil 2013). Thus, as a biocide, it can be considered as more environmentally friendly and has lower mammalian toxicity when compared to others.

Decay fungi and subterranean termite resistance of particleboard treated with sodium fluoride have been previously reported (Tascioglu *et al*. 2017). The in-line treatment with sodium fluoride, up to 3% treatment based on wood particle weight significantly improved decay fungi and termite resistance of particleboards without any negative effect on physical and mechanical properties. The robust leaching procedure, on the other hand, partially affected this resistance due to relatively high leachability of sodium fluoride in water.

Most of biological resistance studies of wood-based composites focus on decay fungi and more common wood-destroying insects such as subterranean termites, this particular work specifically investigates biological resistance of sodium fluoride incorporated particleboard against mold fungi and *Hylotrupes bajulus* (L.) larval activity in the laboratory conditions.

EXPERIMENTAL

Board Manufacturing

Particles obtained from demolished construction materials were used for board manufacturing. The untreated mixed wood species had an average moisture content of 6-7% at the time of manufacturing. A white powder form of sodium fluoride (NaF) (99% purity, from Nacalai Tesque Inc., Kyoto, Japan) was mixed with wood particles at four different target retentions (0, 1, 1.5, and 3% of the total particle weight) in the blender. Polymeric diphenylmethane diisocyanate resin (pMDI) was sprayed after the wood particles were blended for 60 s. The resin amount applied was at the level of 10% of the total wood particle weight. The experimental boards in 300 x 300 mm size were hand formed as a single layer form in a wooden forming box before hot pressing at 160 °C for 10 min. The target thickness and density of the boards were 15 mm and 700 kg/m^3, respectively. No wax or any other chemical was utilized during the manufacturing process. Three replicates for each retention level were pressed, totaling 12 boards including 0% sodium fluoride controls. The specimens for mold and larval tests were cut from those boards after conditioning at 22 °C and 60% relative humidity for 3 weeks.

Leaching Test

To test the effects of leaching on NaF retention and mold and old house borer larvae resistance of the boards, a robust leaching procedure was applied to additional sets of specimens according to the Japanese Industrial Standards of Quantitative standards and testing of wood preservatives (JIS K 1571 2010). The specimens were exposed to 10 cycles of leaching by immersion in deionized water at 10 times the amount of the specimen volume. The water was stirred with a magnetic stirrer at 400 to 450 rpm for 8 h followed by a 16 h drying period in a circulating-type oven at 60 °C. The whole process took 10 days. The large leaching water volume was intentionally used to create an aggressive leaching environment.

Laboratory Mold Tests

Mold resistance tests were performed in accordance to the ASTM D4445 standard test method (ASTM 2010). A mixed mold spore suspension of the three mold fungi, *Aspergillus niger* Tiegh. (Wilcox 117), *Trichoderma harzianum* Rifai (HAMBI 2678), and *Penicillium pinophilum* Hedgc., (HAMBI 2894) was prepared by washing the surface of individual 2-week-old Petri plate cultures with 10-15 mL of sterile deionized water. Washings were combined in a spray bottle and diluted to approximately 100 mL with DI water to yield approximately $3x10^7$ spores mL^{-1}. The spray bottle was adjusted to deliver 1 mL inoculum per spray. Specimens were sprayed with 1 mL of mixed mold spore suspension and incubated at (27 ± 2) °C and 80 % ± 5 % RH for 4 weeks. After 1, 2, 3, and 4 week incubation, specimens were visually rated for the extent and intensity of mold growth on a scale of 0 to 5, with 0 indicating that the specimen was completely free of mold growth and 5 indicating that the specimen was completely covered with mold growth. The moisture content of samples was measured at the end of the 4-week test. Four randomly selected specimens 30 (L) x 30 (W) x 15 (T) mm in sizes from each retention level were tested for mold resistance. An additional set of Scots pine solid wood specimens were also included to observe mold inoculum growth on solid wood surface under the same conditions. The total number of specimens was 60 for mold resistance test including untreated solid wood reference specimens.

Laboratory Larvae Tests

EN 47 standards were used to test treated and untreated particleboard specimens against Old House Borer [(*Hylotrupes bajulus* (L.), (Coleoptera:Cerambycidae)] larvae. An addition set of leached specimens from treated particleboards and Scots pine (*Pinus sylvestris*) sap wood reference material were also prepared for comparison reasons. Specimens in 50 x 25 x 15 mm size were cut from 300 x 300 manufactured particleboards. Each particleboard and solid wood reference specimen was prepared with a drilled hole 3.5 mm width and 22 mm in depth before conditioned at 20 °C and 65% RH for 4 weeks (EN 47 2016).

The test larvae were obtained from eggs produced from mating adult *H. bajulus* insects in laboratory conditions in Forest Biology and Wood Protection Laboratory of Duzce University. The larvae were matured 5 months on Scotts pine sapwood feeder blocks before delicately being taken out. All larvae were weighed with an electronic balance, and only the ones with the closest weight (between 60 and 90 mg) were used for the testing. After each larva was introduced into the predrilled hole in a head-down position, the hole openings were plugged with piece of cotton wool. The test blocks then were transferred into a conditioned environment kept at 27 °C and 80% RH for 16 weeks. At the end of test period the particleboard blocks were opened to remove larvae. For each group, the mortality rates of larvae were calculated. For each treatment level (4 levels including untreated controls) 6 replicates were tested. Including unleached, leached and Scots pine sapwood specimens the total specimen number was 54 for this test.

RESULTS AND DISCUSSIONS

Laboratory Mold Tests

Mold resistance of particleboard that had been incorporated with NaF, as well as untreated solid wood reference specimens were visually rated after being exposed to mold fungi for 7, 14, 21, and 30 days respectively. Figure 1 shows mold rating of tested specimens (A: unleached, B: leached) against the exposure time. Reference Scots pine sapwood specimens resulted in the highest mold ratings as 4 and 4.8 respectively in both tests, indicating that the mold fungi used in the test was active. In general, regardless of the leaching process, untreated control (0% NaF) specimens gave the highest mold ratings at the end of the exposure period, 3.5 for unleached and 4.5 for the leached specimens, respectively.

Mold ratings started to significantly decrease with increasing NaF retention in the tested boards, whether unleached or leached specimens were concerned. For example, the lowest mold growth rating was 1, and this results was recorded for the highest NaF retention (3%) for unleached specimens at the end of 4 week exposure period. The leaching process seemed to have a minor effect on mold ratings since the highest mold rating increased to 1.5 at the end of the same period. This indicates that unlike the decay fungi and termite tests, the remaining NaF amount after leaching process was high enough to suppress mold fungi activity (Tascioglu *et al.* 2017). As a result, higher retentions (higher than 3% NaF) might fully eliminate mold activity in particleboards even in wet environments.

Laboratory Larvae Tests

Based on data obtained from the experiment, none of *H. bajulus* larvae survived at any retention level including untreated control particleboards at the end of test period with the exception of a single larva on the leached control specimen (Fig. 2). This clearly indicates that with or without NaF treatment the particleboard environment tested is not favorable for *H. bajulus* larvae survival. Thus, the effect of biocide inclusion on larvae deaths was unclear. Solid Scots pine specimens, on the other hand resulted in zero percent mortality at the end of the same test indicating the test larvae are healthy and active.

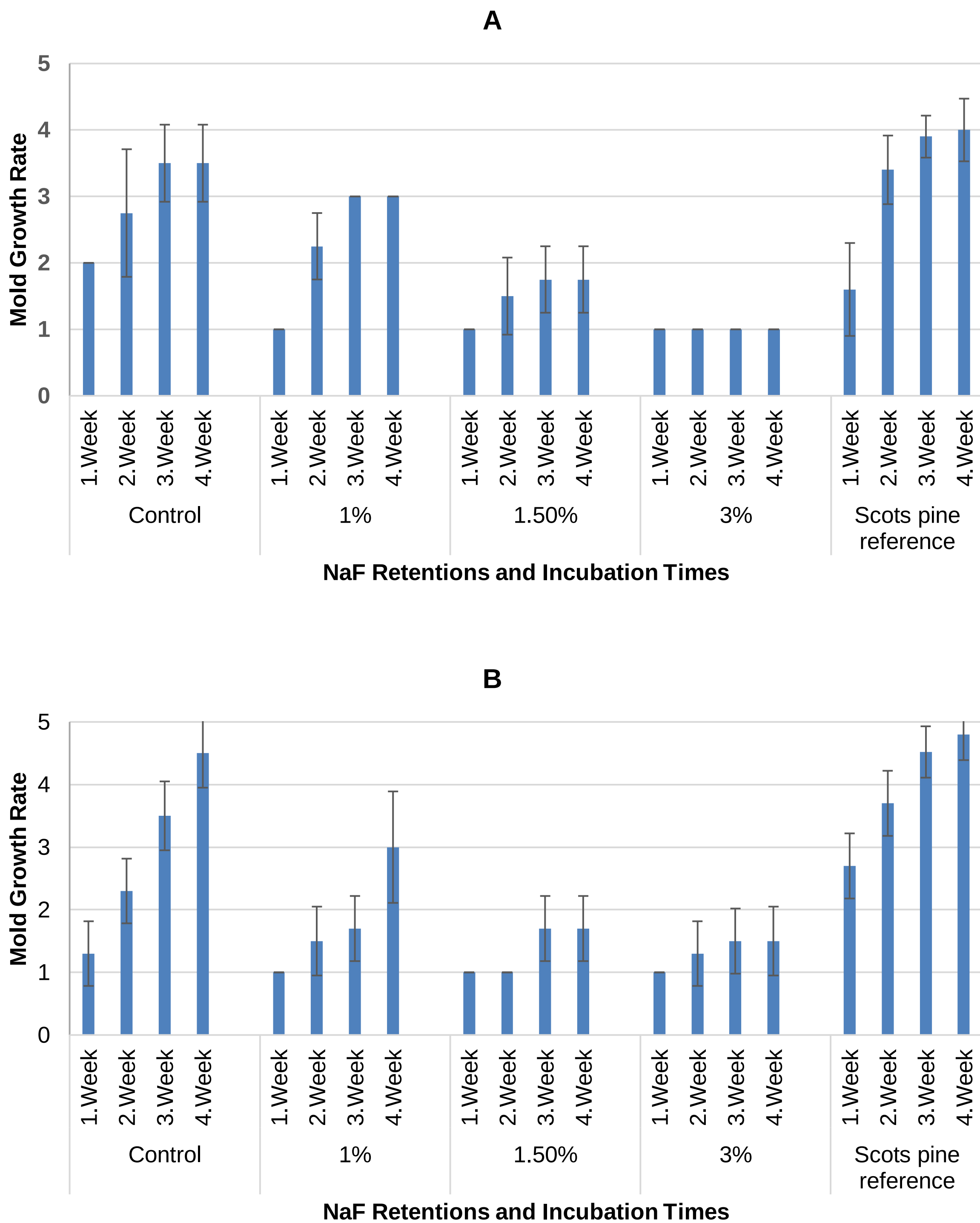

Fig. 1. Mold resistance of NaF incorporated particleboard (A: unleached specimens, B: leached specimens). (Scots pine sapwood specimens were used as reference material and were not exposed to the leaching procedure).

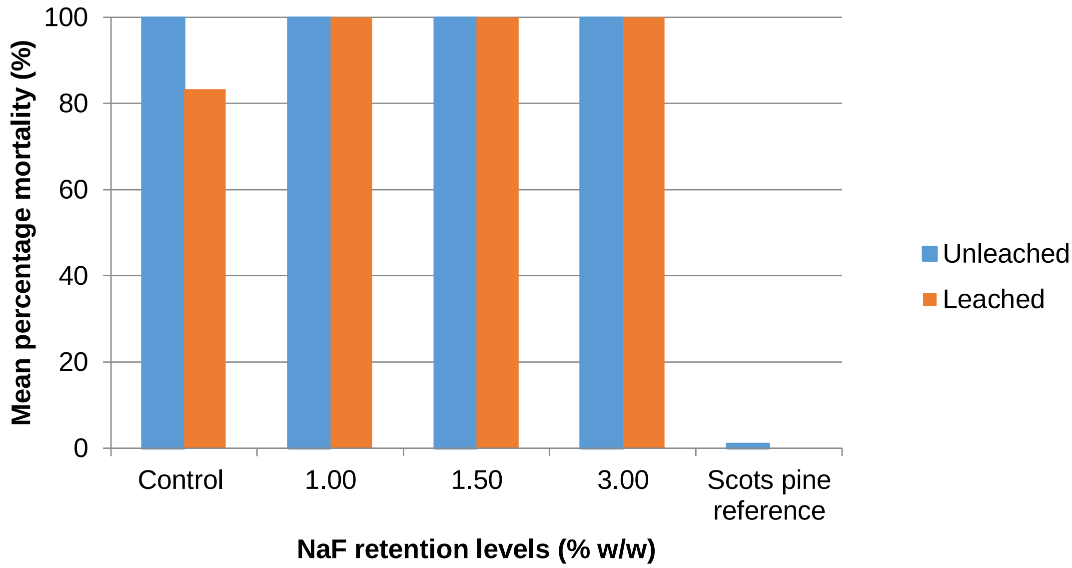

Fig. 2. Mean percent mortality of *H. bajulus* larvae in particleboard treated with NaF at the end of a 16 weeks test period (Scots pine sapwood specimens used as reference material and did not exposed to the leaching procedure)

The mixed wood species used to manufacture the test specimens having a relatively high percentage of adhesive amount or a specific ingredient of the adhesive might hamper feeding behavior of the larvae and cause very high mortality rates in the particleboard environment. While there are no direct references to the anti-fungal or anti-insect properties of pMDI adhesive used in wood-based composites industry, formaldehyde, a subcomponent of melamine-urea-formaldehyde (MUF) resin commonly used in wood-based composites, has been expressed to suppress fungal activity (Yalinkilic *et al.* 1998). Slight reduction in mortality rate (83.3%) in leached control might be explained with the robust nature of leaching process which removes some of toxic extractives or chemicals from wood or adhesive portion of the wood-based composite material tested. Furthermore, a similar study compares antifeedant and repellent rates of solid wood (*Eucalyptus urograndis* and *Melaleuca leucadendra*) and medium density fiberboard (MDF, another very common wood-based composite) manufactured from the same species against larvae of Japanese pine sawyer beetle and pine shoot beetle (Xu *et al.* 2013). They reported that repellent rates increased from 53.5% and 59 % for solid wood of the mentioned wood species to approx. 77% for MDF specimens of the same species, respectively. Similar increases have also been reported for antifeedant rates of both larvae when the solid wood and MDF specimens compared. It was concluded that wood-based composite (MDF) had a superior repellent ability to the tested larvae when compared to solid wood. They related this phenomenon to urea-formaldehyde adhesive or other additives used in MDF manufacturing may release various odors or low-concentration toxic substances to repel the test insects.

CONCLUSONS

1. The incorporation of NaF as a biocide via in-process treatment was determined to be beneficial for the protection of particleboards from mold activity in unleached and even in leached environments.
2. The increase in NaF retention levels from 1% to 3% helped significantly reduce mold activity on particleboard surfaces.
3. The robust leaching process caused only slight increase on mold growth rates, indicating remaining biocide within the leached specimens was high enough to suppress mold activity.
4. The pMDI resin particleboard in unleached condition showed 100% mean mortality on *H. bajulus* (L.) larvae. The environment within the material seemed to be inappropriate for larvacidial survival, thus the effect of added biocide was unclear.

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