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Resistance of modified wood to marine borers

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ABSTRACT

The resistance of differently modified wood to the common shipworm, *Teredo navalis*, and the wood boring crustacean, *Limnoria quadripunctata*, was assessed in a field trial and by means of a short term laboratory assay, respectively. Scots pine (*Pinus sylvestris*) sapwood was treated with TEOS (tetra-ethoxy-ortho-silane) and different thermosetting resins, namely phenol formaldehyde (PF) and methylated melamine formaldehyde (MMF). Additionally, acetylated and untreated Radiata pine (*Pinus radiata*) was included. In the field trial according to EN 275 in the Baltic Sea over a period of six years the specimens were exclusively attacked by *T. navalis*. For the laboratory assay, matchstick-sized samples cut from spare panels prepared for the field trial were subjected to individuals of *L. quadripunctata*; faecal pellet production served as a measure of feeding rate. Treatments that prevented shipworm attack in the field also reduced feeding of *L. quadripunctata* in the laboratory assay: efficacy of resin treatments was enhanced by parameters that increase the amount of resin in the cell wall (i.e. high WPG and dry curing conditions); acetylation resulted in high resistance; and TEOS treatment was not effective. The results suggest that modification on cell wall level is required to impart marine borer resistance.

1. Introduction

Wood has a number of advantages that make it a competitive material for waterfront structures such as groynes, jetties, and dolphins (Crossman and Simm, 2004). The service life of such structures, however, is often limited due to degradation of the below water portions (use class 5; EN 335, 2007) by marine borers. In temperate waters, two types of borers cause significant damage: teredinids (shipworms) and limnoriids (gribbles) (Oliver, 1974). Attack by these organisms is traditionally prevented by treating wood with biocidal wood preservatives or by using tropical timber species that are naturally resistant. The use of biocidal wood preservatives, however, has been legally restricted during implementation of the Biocidal Products Directive (1998) and resistant timbers with a proven track record are poorly available in large dimensions required for many applications. Moreover, there are environmental concerns regarding the utilization of such timbers as it might contribute to tropical deforestation (Williams et al., 2004). Plastic barriers can effectively protect wood piles from shipworms, but installation is costly and barriers are often susceptible to mechanical damage that exposes unprotected wood (Morrell et al., 1984).

Wood modification might be an alternative to protect European species or plantation grown timbers in marine environments, because, by definition, modified wood is non-toxic and does not release toxic substances during service or disposal (Hill, 2011). Wood modification involves various methods to improve dimensional stability, durability, weathering resistance, etc. Most modification processes are based on the application of heat (thermal modification), chemical reaction of cell wall polymers with a reactant (chemical modification) or deposition of the modification agent within the wood substance (impregnation modification). Impregnation modification with an agent that does not penetrate the cell wall is referred to as lumen treatment.

Early studies on chemically modified wood suggested that acetylation increases resistance to marine borers (Tarkow et al., 1955; Johnson and Rowell, 1988); but in another test acetylated wood failed after only two years due to attack by both teredenids and limnoriids (Larsson Brelid et al., 2000). In the most extensive

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marine trial on differently modified wood to date limnoriids were hardly active so that only shipworm resistance was tested (Westin et al. 2006). This trial confirmed improved resistance of acetylated wood (Larsson Brelid and Westin, 2010), with weight percent gains (WPG: percentage increase in dry mass due to modification) being ca. 20% in all studies mentioned. In the same study, chemical modification by maleoylation and succinylation did not increase shipworm resistance, while impregnation modification with furfuryl alcohol and methylated melamine formaldehyde (MMF) prevented attack at WPGs higher than 20%. Thermal modification and lumen treatment with oil did not impart resistance.

In all the studies mentioned above, marine borer resistance has been assessed using a marine field trial. These trials usually need to extend over several years to generate meaningful findings; according to EN 275 (1992) results should be interpreted only after a minimum period of five years. Furthermore, a test site with an active population of both teredinids and limnoriids is required to reliably predict durability in European marine waters. Due to the life cycle and dispersal strategy of limnoriids, attack by this group of borers is not guaranteed at many sites. Therefore, Borges et al. (2009) developed a short term laboratory assay for measuring feeding of *Limnoria* under forced feeding conditions. Using this assay, modification with DMDHEU (dimethylol-dihydroxy-ethylene-urea) (Borges et al., 2004) and acetylation (Papadopoulos et al., 2008) were shown to reduce the feeding rate of *Limnoria quadripunctata*.

This study investigates the resistance of differently modified wood to marine borers. It focuses on impregnation modification with thermosetting resins, but it also includes acetylated wood and silica containing wood. Shipworm resistance is assessed in a marine field trial in the Baltic Sea with a duration of six years. No limnoriids were active at the test site. Therefore, resistance to limnoriids was tested using the laboratory assay developed by Borges et al. (2009).

2. Materials and methods

2.1. Wood treatment

Except for acetylation, all treatments investigated in this study (Table 1) were applied to Scots pine (*Pinus sylvestris* L.) sapwood. Wood was modified with two thermosetting resins: methylated melamine formaldehyde (MMF, Madurit® MW 840/75WA; INEOS Melamines, Frankfurt am Main, Germany), and phenol formaldehyde (PF, Phenodur® PR 635/78WA, Allnex Germany GmbH, Wiesbaden, Germany, M_n = ca. 400 g mol^{-1}). Modification with MMF 10% was carried out on a pilot plant (Krause, 2008; process 5). For lab scale modification with MMF 25% and PF 25% the impregnated specimens were cured and dried in an oven. MMF 25% treated specimens were dried and cured simultaneously (dry curing; Klüppel and Mai, 2013). PF 25% treated specimens were wrapped in polyethylene terephtalate (PET) for curing and subsequently dried (wet curing) because dry curing led to severe cracking.

Tetra-ethoxy-ortho-silane (TEOS, Dynasilan A®, Evonik Industries AG, Rheinfelden, Germany) was applied in sol state as described by Donath et al. (2004). Titan Wood B.V. (Arnhem, Netherlands) supplied Accoya®, which is Radiata pine (*Pinus radiata* D. Don) chemically modified with acetic anhydride. Reference specimens were treated with acid copper chromate composed of 30% (m/m) CuO and 70% (m/m) CrO_3. Concentrations of the preservative solution were chosen to result in retentions of copper and chromium comparable to the reference treatments suggested in the European standard EN 275 (1992). The preservative treated specimens were stored at room temperature for 8 weeks to ensure fixation of the chemical.

Specimens for the laboratory assay were cut from spare panels prepared for the field test, except for the PF-modified wood. While PF-modified panels for the field test were cured wet, specimens for the laboratory assay were cut from dry cured panels (Klüppel and Mai, 2013). Although dry curing led to severe cracking, sound specimens needed for laboratory could be produced from these panels.

2.2. Field trial

2.2.1. Installation and evaluation

When wood was modified on lab scale, panels measuring 200 × 75 × 25 mm^3 (l × r × t) were treated. Accoya® and MMF (10%) treated specimens were cut from boards after treatment. Ten specimens of each treatment were prepared with a hole of 16 mm in diameter in the middle and attached to ladder-like racks made of construction steel similar to the arrangement described in Annex A of EN 275 (1992). Plastic tubes of 25 mm length served as spacers between the specimens.

The racks were exposed in the Baltic Sea (Hejlsminde, Denmark; 55° 21′ N, 9° 36′ E) at 2 … 4 m below medium high tide. Salinity at the test site ranges between 15 PSU and 25 PSU (practical salinity unit; corresponds to 1.5 … 2.5%). Water temperature varies between 0 … 5 °C in January and 20 … 25 °C in August with four to five months per year above the common shipworm's spawning temperature of 14 °C (Nair and Saaraswathy, 1971; NERI, 2009).

The exposure started in May 2008; PF-treated specimens were included in 2010. Samples were examined annually in winter or spring. At each inspection, the fouling on differently treated samples was compared visually. Then the fouling organisms were carefully removed with a scraper and the specimens were X-rayed and reinstalled in the water. Each specimen was rated according to the European standard EN 275 (Table 2). For each treatment, the ratings of all test specimens were added up and divided by the respective number of replicates to obtain a notional average rating.

Table 1
Modification agent, WPG (percentage increase in mass due to modification) and curing conditions of treatments investigated in this study; where different WPGs were adjusted by changing chemical concentration of the impregnation solution, this concentration is included in the treatment name; % (m/m).

Treatment	Chemical	Approximate mean WPG		Curing conditions
Accoya®	Acetylated Radiata pine	>20%		–
MMF 10%	Methylated melamine formaldehyde	10%		kiln (mild)
MMF 25%		25%		oven (dry)
PF 25%	Phenol formaldehyde	35%	Field trial:	oven (dry)
			Lab. assay:	oven (wet)
TEOS	Tetra-ethoxy-ortho-silane	25%		–
CC 0.6%	CuO (30%); CrO_3(70%)	3.5 kg/m^3		–
CC 2.5%		15 kg/m^3		–