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Brief Report

Biological Resistance of Acetylated Radiata Pine, European Beech, and MDF against Marine Borers at Three Italian Sites after Five Years Immersion

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Abstract: The aim of this research was to determine the resistance of acetylated wood against marine biodeterioration in use class 5 for use in temperate waters. The resistance of acetylated radiata pine (*Pinus radiata* D. Don) on solid and medium-density fiberboard (MDF) panels was compared with untreated wood of European species, such as European beech (*Fagus sylvatica* L.), sweet chestnut (*Castanea sativa* Mill.), European oak (*Quercus robur* L.), and marine plywood. As a reference control, untreated Scots pine (*Pinus sylvestris* L.) sapwood was used. The field tests were carried out in accordance with EN 275, and started in April 2015. The three Italian exposure sites were Marine of Scarlino private harbor, Port of Genoa, and the Venice Lagoon. Final evaluation in 2021 showed a greater resistance to marine borers of acetylated wood, radiata pine, and beech and MDF panels. However, the untreated European species showed low resistance against marine organisms, with complete decay after the first year of exposure.

Keywords: acetylation; wood modification; inherent resistance

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1. Introduction

Acetylation of wood is a chemical process described since the beginning of the 20th century. Research efforts since the late 1980s and 1990s have led to the scaling up of this process.

It consists of an impregnation of acetic anhydride, followed by a heating process to start the exothermic reaction, i.e., the acetylation of carboxylic groups of wood with the production of acetic acid. After this reaction, the mixture of acetic acid/acetic anhydride is removed from the wood [1]. Several theories have been proposed to explain the high resistance of acetylated wood to fungal attacks, which are reviewed by Sanders et al. [2]. One theory is that enzyme penetration is prevented by physical blocking in the cell wall micropores. Another theory is based on moisture exclusion; in other words, the equilibrium moisture content of highly acetylated wood is too low to support fungal attacks. A third possible mechanism described in this review is the lack of enzyme accessibility in the acetylated wood cells. The most recent accepted theory, as described in the above-cited review, is a combination of difficulty in recognizing the substrate by enzymes of fungi, and the lower moisture content of acetylated wood.

The commercial development of acetylated timber arose in Europe with the construction of a pilot plant in Arnhem, the Netherlands. This first attempt was unsuccessful, but the equipment and intellectual property were taken over by Accsys Technologies PLC, who formed a company called Titan Wood Technology PLC. This company started the first commercialization of acetylation of wood in 2007, with a productivity of 30.000 m^3 [3]. The production during the years increased to 60.000 m^3 by 2018 [4].

Acetylated Scots pine (*Pinus sylvestris* L.) wood samples were tested in ground contact (stake test) at two Scandinavian test sites, according to European standard EN 252 [5]. The resistance to fungal decay for highly acetylated wood (around 21% acetyl) is of the same magnitude as for CCA-treated wood at high retention level. Acetylated wood samples were also tested in seawater on the Swedish west coast for resistance to marine borers. The results showed only minor protection against marine borers, although the degree of attack was reduced with increasing content of acetyl groups [6,7].

The aim of this research work was to determine the resistance of commercially produced acetylated wood against marine organisms, in use class 5 according EN 335 [8] (in marine water). The resistance of acetylated radiata pine has been compared with that of untreated woods (radiata pine, Scots pine sapwood, European beech, European oak heartwood, and sweet chestnut heartwood). A further two wood-based products were tested; gaboon (*Aucoumea klaineana* Pierre) plywood was compared with an acetylated medium-density fiberboard (MDF) panel. The method was based on European standard EN 275, which evaluates the resistance against marine organisms in temperate waters [9].

2. Materials and Methods

The experimental method for studying the biological resistance of acetylated wood supplied by Accoya was the European standard CEN EN 275 [9]. The aim of this standard is to determine the relative effectiveness of wood preservatives applied by vacuum pressure impregnation. This method, as indicated in CEN EN 350 [10], is also used for determining the natural durability, of wood-based materials, which also includes modified wood.

This standard was used to determine the conferred durability by the Accoya acetylation process on radiata pine and on European beech.

The wood species used as reference (i.e., untreated) were radiata pine, Scots pine, European beech, European oak, and sweet chestnut. A further two wood-based products, marine plywood and gaboon, 25 mm thick, were used as reference products for marine use, and an acetylated MDF panel of 18 mm thick. The dimensions of the samples were $200 \pm 1 \times 75 \pm 1 \times 25 \pm 1$ mm at $12 \pm 2\%$ wood moisture w/w %.

During the test, new untreated controls of Scots pine were added each year to replace heavily tunneled control panels.

The experiment was performed at three Italian marine sites: Genoa, at CNR IAS experimental field station; Marina di Scarlino (Grosseto), in a private harbor; and Venice, at CNR ISMAR docks.

The Genova Experimental Marine Station (GEMS) of CNR IAS is placed inside the Genova harbor. It is included in the MARS network (The European Network of Marine Research Institutes and Stations), and is widely used for EU and national research projects, and by companies for ISO/ASTM tests. The geographical coordinates, the average water temperatures (°C), and the salinity (PSU) of the three stations are reported in Table 1.

The Marina di Scarlino is a private harbor near Follonica, Grosseto.

The Venice station is located inside the historic Arsenal of Venice, a protected harbor receiving euhaline waters of the Venice Lagoon. The rack was hung on the floating mooring pontoon at a depth of one meter from the water surface.

The salinity of the water was measured in the sites where the racks were placed under the surface, and the averages refer to the summer season.

Each set was made up of ten replicates of commercially produced acetylated Pinus radiata, three replicates of untreated radiata pine, five specimens of untreated sapwood of Scots pine (reference control), five replicates of untreated sweet chestnut, five replicates of untreated European oak, three replicates exterior-grade gaboon plywood 25 mm thick, and three replicates of acetylated MDF panel. In total, 37 specimens were mounted on a nylon rack and submerged at each test site.

The evaluations were carried out every year for five years over the period of March 2016 to October 2021 (Table 2). The evaluation in 2020 was not conducted due to the COVID-19 lockdown. After the last evaluation, the racks were dismantled.

Table 1. Averages of seasonal temperatures and salinity at the three sites.

Station and Coordinate	Winter Mean Temperature (°C) (January, February, March)	Spring Mean Temperature (°C) (April, May, June)	Summer Mean Temperature (°C) (July, August, September)	Fall Mean Temperature (°C) (October, November, December)	Mean Salinity in Summer (PSU)
CNR IAS experimental field station (44°24′ N 8°56′ E) GENOA	13.8 ± 0.8	18.0 ± 3.4	25.0 ± 0.6	18.0 ± 3.1	37.8 ± 0.6
Marina di Scarlino (42°53′7.15″ N, 10°46′59.05″ E) GROSSETO	14.1 ± 0.4	18.5 ± 3.4	24.6 ± 0.9	18.7 ± 2.5	34.4 ± 1.4
CNR ISMAR docks (45°26′14.26″ N, 12°21′18.51″ E) VENICE	8.5 ± 2.3	20.4 ± 4.3	25.8 ± 2.3	13.1 ± 4.5	30.4 ± 2.0

Table 2. Evaluation dates of racks. In brackets are the cumulative days of immersion.

Site	2015	2016	2017	2018	2019	2021
Venice	1 April	17 February (308)	13 April (729)	23 April (1104)	19 April (1465)	18 June (2195)
Genoa	1st April	1 February (306)	6 April (736)	7 May (1132)	2 May (1492)	6 October (2227)
Scarlino	1st April	25 January (299)	7 April (737)	11 April (1106)	9 April (1469)	18 May (2239)

The evaluations were carried out by raising the racks, cleaning the samples, and inspecting the wood surface for Limnoria tunnels. The decay caused by shipworm tunnels was quantified through radiographic imagery. The radiograph utilized for analyzing the samples was a Gilardoni Radiolight applied at 50 kV, 3 mA, 3 min of exposition. The X-ray films were Carestream M100, dimensions 18 × 24 cm^2, the developing and fixing solution were Carestream Single Part. Times taken in developing and fixing of film were, respectively, 5 min and 3 min. The data for the evaluations carried out are reported in Table 2. The decay ranking was based on a four-grade rating system, according to the percentage of surface attacked, from 0 (sound) to 4 (failure, more than 50%), through 1 (slight decay, not more than 15%), 2 (moderate decay, not more than 25%), and 3 (severe decay, between 25% and 50%), as reported in Table 3. The evaluation in 2020 was skipped due to the COVID-19 lockdown. After the last evaluation, the racks were dismantled. The determination of shipworm species at the different sites was carried out via morphologic identification, as described by Turner [11], and using an optic microscope.

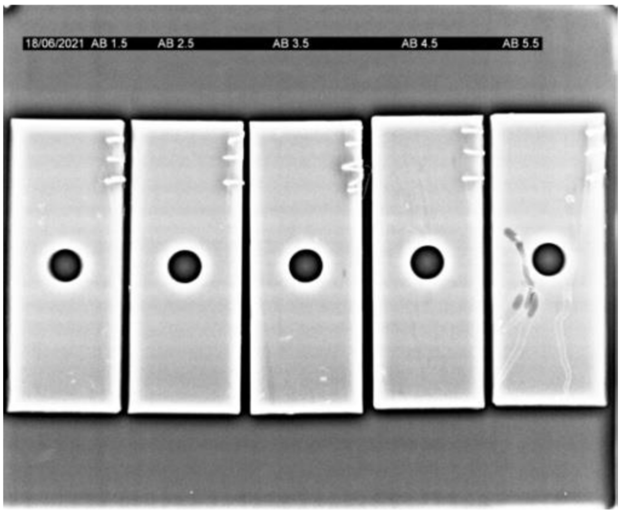
Table 3. Rating system for attack by teredinids according to EN 275.

Rating	Classification	Condition and Appearance of Test Specimen on the X-ray Film
0	No attack	No sign of attack
1	Slight attack	Single or a few scattered tunnels covering not more than 15% of the area of the specimen
2	Moderate attack	Tunnels covering not more than about 25% of the area of the test specimen
3	Severe attack	Tunnels covering between 25% and 50% of the area of the specimen
4	Failure	Tunnels covering more than 50% of the area of the specimen

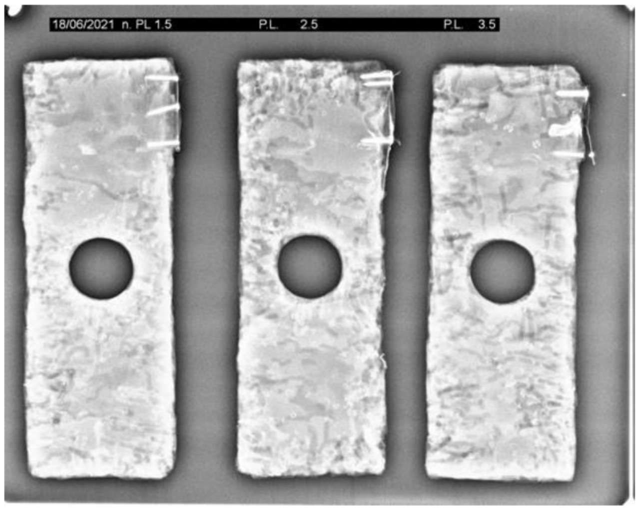
3. Results and Discussion

The results from the evaluation of 2016 and 2017 are already reported in a previous paper [12]. In this paper, it was reported that, after only two years of exposure at all the Italian sites, the non-durable reference control species, untreated beech and radiata pine, and wood species European oak and sweet chestnut, were heavily attacked by marine organisms. The acetylated Scots pine and European beech in solid wood and MDF were, in contrast, completely sound. The marine plywood samples were attached, but not to more than 50% of the surface.

The final results obtained after five years provide evidence that all the acetylated radiata pine and MDF were completely sound; the acetylated European beech, in few cases, showed some shipworm attack; and the marine plywood was thoroughly attacked. The untreated pine did not resist more than one year at any of the sites. Figure 1a,b shows the radiographs of acetylated beech and MDF panel samples in the last evaluation.



(**a**)



(**b**)

Figure 1. (**a**) Set of acetylated European beech samples; (**b**) set of acetylated MDF samples, from the last evaluation in Venice.

The final results obtained after five years evidenced that all the acetylated radiata pine and MDF were still completely sound; the acetylated European beech, in few cases, showed some shipworm attack; and the marine plywood was thoroughly attacked. The untreated pine did not resist more than one year at any of the sites. Table 4 shows the average results after five years.

Table 4. Results expressed as nominal value in accordance with EN 275:1992.

Treatments	Venice (Average)	Scarlino (Average)	Follonica (Average)
Acetylated radiata pine	0	0.38	0
Acetylated European beech	0.40	0.20	2
MDF	0	0	0.43
Marine plywood	4	4	4

Tunnels of Limnoria were found only on untreated Scots pine samples in the first evaluation in Genoa and in Marina di Scarlino. The species of *Limnoria* was not determined (Figure 2).

Figure 2. *Limnoria* sp. on immersed Scots pine sapwood at Marina di Scarlino.

In Venice, *Limnoria tripunctata* Menzies, 1951 and *Limnoria tuberculate* Sowinsky, 1884, and *Chelura terebrans* Philippi, 1839 were identified.

The attacks made by crustacean species on the Scots pine samples were non-significant compared to the attacks by teredinids; this could be due to the tolerance of teredinids species to a wider range of salinities and temperature [13].

Borges, 2014 et al. reported a wider distribution range of *L. lignorum* Rathke, 1799 in Europe relative to *L. quadripunctata* Holthuis, 1949and *L. tripunctata*; this may be explained, in part, by the wider range of salinities tolerated by *L. lignorum* L. (17–35 PSU), and/or, as Borges reported, to erroneous species identification in the past [14].

The results obtained for the untreated Scots pine samples confirmed that in most of the European coastal sites, there was a higher hazard posed by teredinids compared to limnoriids. On other hand, the higher hazard presented by limnoriids in Portugal confirms that limnoriids should not be underestimated regarding their activity.

Borges et al. [15], in their survey identifying the teredinid species of European coastal waters, found nine teredinid species that were established, and two alien species. Teredo navalis and Nototeredo norvagica were the species with the widest distribution. Furthermore, *L. pedicellatus* Quatrefages, 1849 and *Bankia carinata* Gray, 1827 were found in the Mediterranean Sea. The species identified in this research are in line with the literature, except for *L. massa* Lamy,1923, found at the Port of Genoa. The teredinid species identified at Genoa were Bankia carinata, Lyrodus massa, Lyrodus pedicellatus, Teredo navalis, and Nototeredo norvagica. Shipworm species recorded in the Arsenal of Venice were *Teredo navalis* L., Lyrodus pedicellatus, and, since the last decade, the alien species Teredo bartschi [16]. At Scarlino, only Nototeredo norvagica and Teredo navalis were found on the samples.

4. Conclusions

The acetylated European beech and radiata pine showed a very high resistance to marine organisms in the various marine conditions, the Port of Genoa, the Venice Lagoon, and the Marina di Scarlino harbor, higher than that of the more naturally durable tropical woods [12]. Furthermore, the acetylated MDF panel had a slightly higher performance compared to marine plywood.

Author Contributions: S.P., D.T. and M.F. represent the scientifically responsible person for, respectively, m Marina di Scarlino, Venice, and Genoa test sites. The other authors contributed, at the same level, towards the experimentation, at a scientific and technical point of view. Part of this paper is presented as proceeding in IRG53, 2022 Bled Slovenia 29 May–2 June. All authors have read and agreed to the published version of the manuscript.

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