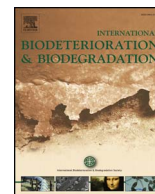




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Weathering of wood coated with semi-clear coating: Study of interactions between photo and biodegradation

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ABSTRACT

In order to clarify the relationship between photodegradation and biological degradation, wood specimens finished with a semi-clear coating were degraded under a xenon lamp for different periods of time. The specimens were then inoculated one of two black stain *fungi* (*Aureobasidium pullulans* and *Epicoccum nigrum*). Colonization was monitored visually and by colorimetric analyses. The extent and the nature of the degradation were evaluated using different techniques. The chemical composition was studied by Fourier Transform Infrared Spectroscopy (FTIR) and the physical changes by both microscopic analyses and adhesion tests. The results obtained from FTIR did not provide relevant information. Coating thickness and adhesion were found to decrease as photodegradation increased. Microscope observations detected numerous bubbles trapped in the coating films. These bubbles were found to become holes following photodegradation and the decrease in coating thickness. It was established that more severe photodegradation led to more extensive colonization of the specimens. The *fungi* seemed to use *transpressorium* to go through the protective layer and take advantage of organic matter present at the wood/coating interface. Fungus colonization was also found to decrease the coating adhesion in the early stages of the exposure process.

1. Introduction

Wood used for outdoor applications such as siding or decking undergoes surface degradation due to a wide range of environmental factors (Evans, 2009; Williams, 2005). The term commonly used to describe this phenomenon is weathering. Weathering includes photodegradation, biodegradation, erosion by water or particles, heat and reaction to pollutants, among others. Studies aiming to clarify weathering mechanisms generally involve laboratory experiments isolating degradation factors (Chedgy et al., 2007; Deflorian et al., 2007; Evans and Banks, 1990; Evans et al., 1996; Kataoka and Kiguchi, 2001; Pandey and Pitman, 2003; Podgorski et al., 1996). Photodegradation is the topic most frequently studied as it is considered the strongest and fastest weathering degradation factor (Davis and Sims, 1983; Feist and Hon, 1984; Hon and Chang, 1984). It is well known that lignin, one of the three main wood polymers, is strongly degraded during photodegradation. Its degradation leads to the production of breakdown products that can facilitate further degradation by other factors (Cogulet et al., 2016; Evans et al., 1996; Leary, 1968; McNally et al., 2005). Another commonly studied factor is the biodegradation of wood

by a variety of organisms (Bardage and Daniel, 1997; Gaylarde et al., 2011; Pandey and Pitman, 2003; Shirakawa et al., 2002; Smith and Swann, 1976; Yilgor et al., 2013). Several studies have focused on wood colonization mechanisms by black stain *fungi*, which are considered the main *fungi* responsible for the colonization of photodegraded wood (Shirakawa et al., 2002). Black stain *fungi* do not affect the structural integrity of wood nor its mechanical performance but the dark coloration affects its aesthetics (Gobakken and Westin, 2008; Ortiz et al., 2014). As a result, the application of new layers of paint or varnish is often required. Both photo and biodegradation lead to decreased product life time and increased maintenance requirements (Dickinson, 1971; Freedonia, 2011; Horvath et al., 1976; Stirling and Morris, 2009; Van den Bulcke et al., 2007).

Studies from the 90s highlight the ability of black stain *fungi* to metabolize lignin breakdown products (Schoeman and Dickinson, 1996, 1997). This particularity can be an issue when transparent finishes are used (MacLeod et al., 1995; Miniutti, 1967; Singh and Dawson, 2003). Penetration through a clear coating film allows light to reach the wood underneath, leading to photodegradation, e.g. lignin degradation. The lignin breakdown products, which are a food source

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for black stain *fungi*, become available at the wood coating interface. The relationship between photodegradation and biodegradation was the focus of the research presented in the present report. Lignin degradation due to photodegradation also leads to the generation of free radicals (Hon and Ifju, 1978; Moore and Owen, 2001). The *fungi* were found to oxidize the mechanical anchorages of the coating, thereby decreasing film adhesion. This can be observed with clear coatings peeling from the wood surface while the protective layer remains undamaged (Evans et al., 2015). Fungal colonization can also lead to decreased coating adhesion by applying pressure onto the coating due to physical expansion. The nature of linkages between the coating and the wood is still under study, but it is widely accepted that mechanical anchorage is the strongest adhesion mechanism.

The objective of this research was to try and elucidate to what extent *fungi* take advantage of photodegradation to grow on wood specimens coated with a semi-clear film. To do so, two hypotheses were assessed. The first hypothesis was that the photodegradation process promotes the growth of black stain *fungi* on wood coated with a semi-clear protection. In order to validate or invalidate this hypothesis, clear-coated wood specimens were degraded under a xenon lamp for different periods of time. The specimens were then inoculated with two black stain *fungi* (*Aureobasidium pullulans* and *Epicoccum nigrum*). Following fungal colonization, they were assessed according to a visual scale (similar to AWWA Standard E24) and colorimetric analysis. In the second hypothesis, photo and biodegradation lead to a decrease in coating adhesion. Adhesion was characterized by means of coating pull-off strength tests. In order to better explain the relationship between photo and biodegradation, the physical and chemical modifications were studied by microscopic analysis and Fourier transform infrared spectroscopy (FTIR) respectively.

2. Materials and methods

2.1. Materials

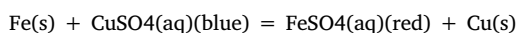
Two batches of white spruce wood (*Picea glauca* (Moench) Voss) were used in this experiment. Both were from sawn woods, but one of them was sanded. As a result, smooth and rough surfaces were obtained. These surfaces were coated with a waterborne paint prepared from a co-emulsion of poly(butylacrylate/methyl methacrylate), p(BA/MMA). The volatile organic compound concentration, as determined by the manufacturer, was 153 g/L. Two layers of paint were applied with a curtain coater. This paint is considered to be a semi-clear protection since it does not mask the wood grain.

2.2. Photodegradation

Coated specimens were exposed under a xenon lamp with a borosilicate filter in a Weather-Ometer Ci3000+ (Atlas, USA). Cycle 1 of ASTM Standard G155 (2013), namely: “operating xenon arc light apparatus for exposure of non-metallic materials” was used. Four test batches of twelve specimens were degraded in the Weather-Ometer for different periods of time. The exposure times ranged from zero exposure to one, two and four weeks.

2.3. Copper sulphate tests

Two layers of paint were applied onto steel panels to form six specimens with around 100 µm of dry film thickness. Three were photodegraded for four weeks in the Weather-Ometer Ci3000+ under the same conditions as for the wood specimens, following which 4 mL of a solution at 10% of copper sulphate (CuSO₄) were poured onto the six coated steel panels. Glass plates were placed over the specimens to allow for the reaction to occur over 24 h (Equation 1).



Any porosity occurring through the thickness of the coating will cause red dots to appear at the steel surface.

2.4. Fungal cultures

Two species of *fungi* causing black stain (usually referred as blue stain in service) were used in this experiment: *Aureobasidium pullulans* and *Epicoccum nigrum*. Different isolates were collected from stained finishes over time and stored. Others were collected from outdoor experiments and grown on 1.5% MEA (Malt Extract Agar). Identification and vigor were confirmed by a mycologist based on morphological characteristics. Several isolates were subcultured on agar plates with a cellophane layer spread on top. Growth was interrupted when the cellophane was fully covered. This aided the collection of fungal mycelium without nutrient agar as potential additional food source for the *fungi*. A final inoculant was prepared using a mix of 25 different isolates of *Aureobasidium pullulans* and another inoculant batch including a mix of 5 different isolates of *Epicoccum nigrum*. The inoculants consisted of harvested mycelium that had been mixed in 200 mL of sterile water in a blender for 3 short pulses of 6 s.

2.5. Inoculation

Before inoculation, the specimens were placed facing down on 1.5% water agar plates (no nutrients) for 7 days at 17 °C and 94% relative humidity in order to increase their water content. The specimens were then removed from the plates and placed on a flat sterile surface in a biosafety cabinet. The inoculation was completed by spraying one batch of specimens with *A. pullulans* and one batch with *E. nigrum* using a hand-held spray bottle until a thin layer of liquid formed on the wood surface. The individual specimens were then placed inside individual plates filled with 3% water agar to ensure that they remained humid. Incubation took place over 14 days at room temperature until growth occurred, and the specimens were rated.

2.6. Experimental design

Fig. 1 shows the experimental design of this research, which identified four different groups of specimens: A, B, C and D that were subjected to different treatments.

2.7. Colonization

Colonization by both *A. pullulans* and *E. nigrum* appeared on the specimens as dark colored hyphal growth. Eventually, colonization took the form of streaking or black stains with a dotted appearance. This characteristic was used to monitor colonization. A visual rating scale was designed based on AWWA E24 (2006): Standard method of evaluating the resistance of wood product surfaces to mold growth. The scale ranged from 0 (no colonization) to 4 (strongest colonization) as described in the complementary file 1. Visual assessment was performed at day 0, 4, 8 and 14, at which point the specimens were placed at 4 °C for the colonization to stop.

2.8. Colorimetric analysis

Both photodegradation and colonization lead to a wood color modification. It was therefore necessary to differentiate the two processes. A colorimeter was employed to do so. The degree of lightness was recorded after either photodegradation alone or combined photodegradation and colonization. Statistical tests served to confirm any differences in the results obtained. The device used was a reflectance spectrophotometer, BYK-Gardner, based on the color scale CIEL*a*b*. The L* axis used for this study represents the lightness and ranges from 0 (pure black) to 100 (pure white).

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