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Evaluation of weathering performance of acetylated hardwood species

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ABSTRACT
Wood is a versatile, natural, and environmentally friendly resource that has attracted attention as a material for sustainable building for many years. In order to enlarge application fields of wood several properties, such as dimensional stability, thermal steadiness, fire resistance, biotic and abiotic degradation resistance or mechanical properties need to be improved. Acetylation is the most well-established treatment when acetic anhydride reacts with hydroxyl groups of cell wall polymers by forming ester bonds. Acetylation improves UV resistance and reduces surface erosion what is important while using wood as façade material. The mechanical strength properties of acetylated wood are not considerably different than not-treated wood, however, its durability is substantially improved. Softwood, mainly Radiata pine, is most used species for commercial acetylation process, nevertheless use of alternative hardwood species is of hight interest. The goal of this research was to comprehensively evaluate the effect of wood acetylation on performance on two hardwood species when exposed to natural weathering. Acetylated wooden boards having a 20% acetyl weight gain on average manufactured from two hardwood: black alder (*Alnus glutinosa* L.), European beech (*Fagus sylvatica* L.), were used for the preparation of experimental samples. The wood modification was performed within the commercial production facilities of Accsys Technologies in the Netherlands. Natural weathering tests were performed for 15 months in San Michele, Italy. Samples were exposed on vertical stands representing a building façade. The stand was oriented to face the southern direction. Differences observed between both species related to surface appearance, erosion, wettability behaviour and changes in chemical composition are important for understanding species-dependent drawbacks of the acetylation process and its further improvement.

INTRODUCTION
All building components that are exposed to environmental elements, including fluctuations in humidity and temperature, rainfall, or ultraviolet radiation, undergo alterations in both appearance and structural integrity (Arpaci et al. 2021; Reinprecht et al. 2017). One major limitation of using unprotected wood on building façades is its aesthetic variation, notably the shift toward a grey tonality due to dark mold growth and UV-induced bleaching (Cogulet et al. 2016; Hill 2006; Pandey 2005). Additionally, the intrinsic variability of wood leads to a non-uniform appearance, and weathering is typically an uneven process resulting in different deterioration rates across various zones of a building (Sandak et al. 2019). Wood may also crack, split, or distort, particularly if the façade is poorly designed or if wooden boards are incorrectly installed (Rüther and Time 2015). Due to their natural composition and intrinsic properties, bio-based materials like wood undergo rapid transformation, prompting the use of various modification methods to minimize degradation from fungal decay and dimensional changes (Williams 2005).
Modification processes enhance specific wood properties using chemical, biological, or physical agents. Chemical modification, such as anhydride treatment, functionalizes the molecular structure of wood polymer constituents, reducing hygroscopicity and enhancing hydrophobicity and dimensional stability (Hill 2000, 2006).

Acetylation, a well-established chemical treatment, involves forming ester bonds with the hydroxy groups of cell wall polymers, significantly improving UV resistance and reducing surface erosion critical for façade materials (Qin et al. 2014; Rüther and Time 2015). The global commercial production of acetylated wood reaches 120,000 m³/year (Jones and Sandberg 2020). Although acetylated wood's mechanical strength properties are comparable to untreated wood, its durability and dimensional stability are greatly enhanced. Despite its initial stability against UV radiation, acetylated wood eventually fades and greys, similar to other woods. As weathering progresses, deacetylation and the effects of dilute acids may increase degradation (Evans 2009). Moreover, acetylated wood remains vulnerable to mold and blue stain fungi since no toxic chemicals are added. However, its improved dimensional stability and resistance to fungal decay enhance the performance of coatings. This research aims to comprehensively evaluate the effect of wood acetylation on two hardwood species exposed to natural weathering, contributing to understanding the drawbacks of the process and suggesting improvements.

MATERIALS AND METHODS

Experimental samples

Acetylated wooden boards with a 20% acetyl weight gain on average, manufactured from the hardwood's black alder (*Alnus glutinosa* L.) and European beech (*Fagus sylvatica* L.) were used for the preparation of experimental samples. Fifty-four small blocks (150 L × 75 W × 20 T mm3, respectively) were cut out from each of the 3 sample types, for 6 natural weathering scenarios and 3 replicas for each test scenario. The wood modification was performed at the commercial production facilities of Accsys Technologies in the Netherlands.

Weathering tests

Natural weathering tests were conducted in San Michele, Italy (46°11'15''N, 11°08'00''E). The purpose of these tests was to gather a reference dataset on material performance over varying exposure durations. Samples were mounted on vertical stands designed to simulate a building façade, facing south. The experiment spanned a total of 15 months. Every three months, three replicas were removed from the stand to halt further deterioration, resulting in a collection of samples exposed for 0, 3, 6, 9, 12, and 15 months. Three replicated samples were measured at each interval representing a distinct experimental scenario. Prior to subsequent measurements, all samples were stored in a climatic chamber maintained at 20°C and 65% RH to ensure stable conditions.

Characterisation methods

Digitalisation

After conditioning samples were scanned with an office scanner HP Scanjet 2710 (300 dpi, 24 bit) and saved as TIF files.

Colour measurement

Colour changes were assessed with a spectrometer following the CIE Lab system, where colour is expressed with three parameters: L* (lightness), a* (red-green tone) and b* (yellow-blue tone). CIE L*a*b* colours were measured using a MicroFlash 200D spectrophotometer (DataColor Int, Lawrenceville, USA). The selected illuminant was D65 and the viewer angle was 10°. Specimens were measured on five randomly selected spots over the weathered surface. The mean values were considered as a representative colour, even if the maximum and minimum readings were preserved to assess the natural variation of the colour distribution.

Microscopic observation and 3D roughness measurement

Keyence VHX-6000 digital microscope (Keyence, Osaka, Japan) was used for microscopic observation, high magnification image acquisition, and 3D surface topography scanning. Colour images were collected with an optical configuration corresponding to ×30 and ×200 magnifications. The light direction and intensity were adjusted to assure a wide dynamic range of the image and avoid generation of saturated pixels. Part of the high magnification images were acquired in the real-time 3D depth reconstruction mode. Data was used to determine surface profile as well as surface roughness indicators.

Contact angle and surface free energy

Dynamic contact angle measurements were performed using the optical tensiometer Attention Theta Flex Auto 4 (Biolin Scientific, Sweden). Five replicates of a sequence with distilled water and formamide were run on each sample using the sessile drop method. The measurement of each drop started at initial contact of the drop with the sample surface and lasted for 20 seconds. The series of images collected were post-processed with the software of the tensiometer. The surface free energy was computed following OWRK/Fowkes method.

RESULTS AND DISCUSSION

The appearance changes in the studied samples after natural weathering at various exposure times are shown in Figure 1. Initially, acetylated samples showed a lightening in color after three months, which then stabilized for the next three months. Photo bleaching of acetylated wood, primarily caused by visible light, progressed, turning in acetylated wood to a grey tonality by the end of the 15-month weathering test.

Biotic attacks often cause spots on the surface, a phenomenon that could be used a rapid homogenization strategy. However, such visual changes are in general viewed negatively on wooden façade claddings. Concurrently with these color changes, all samples also displayed minor surface disintegration, including raised fibers and small cracks (Žlahtič 2016).

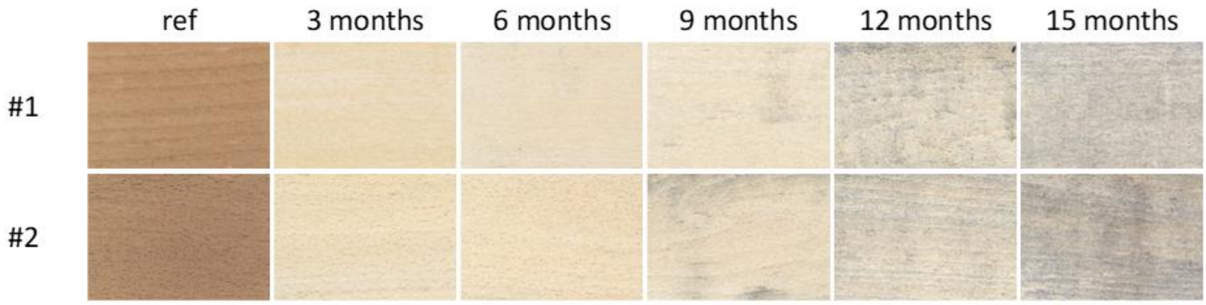

Figure 1: Coloured scanning electron micrograph of ash cross-section (a) and the centre of the same cross-section enlarged and rotated by 180° (b). #1 black alder, #2 European beech

Figure 2 presents colourimetry changes of acetylated wood samples exposed to natural weathering. The apparent lightness (CIE L*) was relatively stable, with only a slight and steady rise at the initial phase of the weathering test. CIE a* gradually decreased for both samples, reaching more stable values from the 6th month of exposure. Values of CIE b* progressively dropped after a slight gradual increase at the beginning of the weathering test.

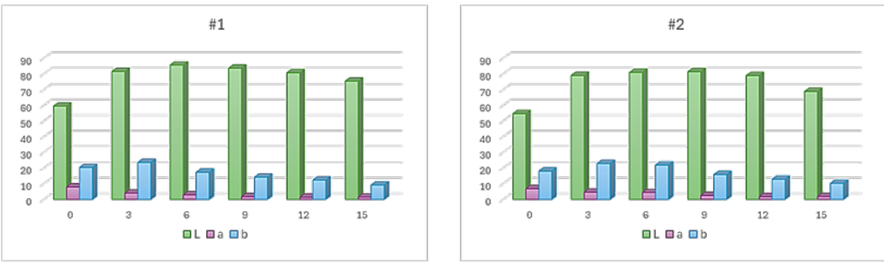

Figure 2: CIE L*a*b* coordinates of acetylated samples exposed to natural weathering. #1 black alder, #2 European beech

Furthermore, a noticeable increase in surface roughness was observed in all acetylated samples. For instance, the surface topography analysis of sample #2 is shown in Figure 3. The 3D topography map, combined with the color image, reveals that hardwood vessels are a primary cause of surface irregularities. Nonetheless, the surface profile outline clearly shows ongoing surface erosion, confirmed by the continuous increase in surface roughness parameters. Three-dimensional (3D) area surface texture assessment is advantageous for characterizing surfaces of heterogeneous and anisotropic materials like wood. The roughness profile (Ra), typically determined from two-dimensional roughness profiles, shows that values of Arithmetical mean surface height (Sa) steadily increased for acetylated alder #1 and beech #2. A steady reduction in skewness (Ssk) suggests a normalization of the top material ratio, indicative of fiber loss and general erosion of the uncoated wood surface. Overall, an increase in surface roughness during weathering corresponds to the removal of individual fibers, leaching of photodegraded components, and overall erosion of the wood surface. Despite the acetylation process generally enhancing mould resistance in wood, acetylated beech (#2) was the most affected by mould growth.

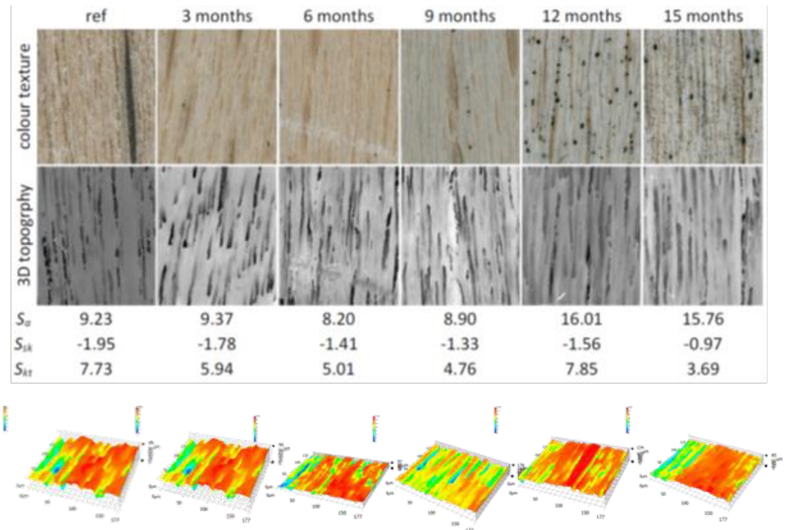

Figure 3: 3D surface topography map, surface profiles, and images of the acetylated beech (#2) exposed 15 months to natural weathering

Regarding the measurement of the dynamic contact angle, a low initial contact angle (θ) was observed in all cases after the weathering process. A drop in θ value occurred after three months, followed by relatively stable values from month 3 to month 15. The estimates of the surface free energy (SFE) are presented in Figure 4, which includes the total surface free energy (γtot) along with its polar (γp) and disperse (γd) components. The values of the SFE for the acetylated species generally fluctuated around 70 mJ·m^{-2}. The values of γp remained fairly constant, while γd showed a drop after the initial 3 months, subsequently oscillating around 15 mJ·m-^{2}. Generally, the weathering process in unprotected wood increases wettability.

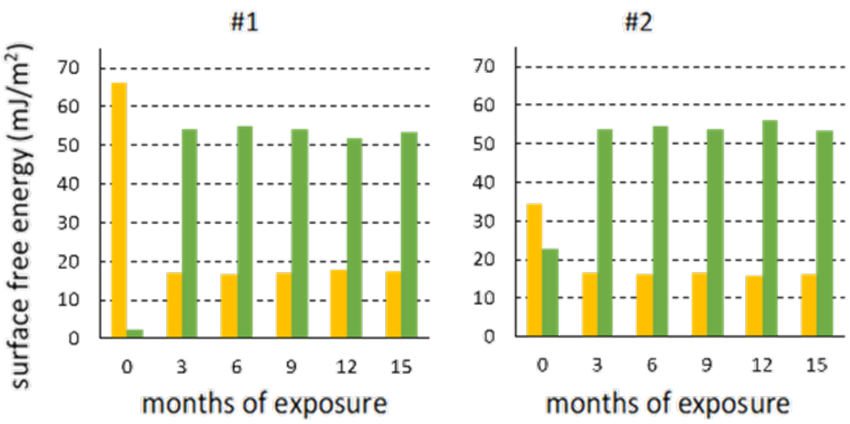

Figure 4: Surface free energy (γtot) including polar (γp) (yellow) and disperse (γd) (green) components. #1 black alder, #2 European beech

CONCLUSIONS

The performance of acetylated wood samples was evaluated using several methods that assess materials at different levels. Although the outward appearance varied, all samples maintained their functionality as cladding material, protecting the building envelope. The grey color and uniform mould growth provided an aesthetic appeal that may be desired by customers. An increase in surface roughness during the weathering process was observed for both hardwoods, associated with the removal of single fibers, leaching of photodegradation components, and general erosion of the wood surface. For both hardwood species, a significant drop in contact angle was observed after three months, followed by relatively stable values from month 3 to month 15. Differences in surface appearance, erosion, wettability behavior, and changes in chemical composition are crucial for understanding species-dependent drawbacks of the acetylation process and its potential for further improvement.

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