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# Weathering of Wood Modified with Acetic Anhydride—Physical, Chemical, and Aesthetical Evaluation

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**Abstract:** The goal of this study is to comprehensively evaluate the natural weathering performance of three wood species representing hardwood and softwood modified with the acetylation process. Alder (*Alnus glutinosa* L.), beech (*Fagus sylvatica* L.), and radiata pine (*Pinus radiata* D. Don) were characterised by various techniques to determine the aesthetical, chemical, and physical changes. The overall aesthetic performance of the investigated species was similar, with all showing a change in appearance after 9 months of exposure. However, the multi-sensor approach used for characterisation revealed differences in weathering behaviour related to surface erosion, wettability, and changes in chemical composition between the investigated species. An increase in the surface roughness observed for both hardwoods was associated with the erosion of the wood surface and the leaching of photodegraded chemical components. On the contrary, values of Sa remained relatively constant for acetylated radiata pine. Acetylated pine wood exhibited lower susceptibility to bleaching at the initial stage of the weathering process (3 months) and represented a more constant CIE L* compared to the investigated hardwood species. The contact angle measured with water gradually decreased in the case of acetylated radiata pine for up to six months, then it plateaued with a slight oscillation around 15°. For both hardwood species, the big drop was observed already after three months, followed by rather similar values. The PCA of IR spectra highlighted different mechanisms in the weathering of acetylated softwood and hardwood. The acetylated hardwood samples showed higher thermal stability than acetylated radiata pine. Experimental findings provide a comprehensive understanding of the long-term performance of acetylated wood, which directly influences its practical applications by enhancing design strategies, maintenance planning, product development, market acceptance, and overall sustainability. Performed tests have demonstrated the potential of underutilised hardwood species, enhanced through the acetylation process, to serve as alternative cladding materials to commonly used acetylated radiata pine.

**Keywords:** wood modification; acetylation; natural weathering; service life performance; multi-sensor characterisation



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## 1. Introduction

All building elements exposed to biotic factors, such as the fluctuation of temperature and humidity, UV radiation, or wetting by rain undergo a change in appearance and structure [1]. The change in appearance, being a consequence of the exposure of un-protected wood, is limiting the use of timber as a cladding material [2]. Unprotected, exposed wood

changes in colour, turning toward grey tonality because of the development of dark mould and due to bleaching as a result of UV. Additionally, the intrinsic variation of wood itself leads to a non-uniform appearance. In most cases, wood weathering is an uneven process, being a consequence of diverse deterioration kinetics occurring in different parts of the facade [3]. Moreover, the cladding may undergo distortion, cracking, or splitting, especially in the case of wrong installation or an incorrect design. The transformation process of wood and other bio-based materials caused by environmental factors is quite fast due to their natural composition and intrinsic properties; therefore, various modification methods are often implemented to minimise degradation related to fungal decay and dimensional changes [4].

Modification processes improve certain wood properties by means of chemical, biological, or physical agents [5]. The chemical modification might act according to two mechanisms. Dimensional stability is improved by the direct cross-linking of the modification agent with the wood cell wall polymers or by the bulking effect, which is the deposition of the reactant in the wood cell wall [6,7].

During anhydride treatment, the molecular structure of wood polymer constituents is functionalised, affecting its hygroscopicity. The wood surface becomes more hydrophobic, and the dimensional stability is enhanced [8]. Acetylation is a commercially developed treatment where acetic anhydride forms ester bonds with the hydroxy groups of the cell wall polymers [9]. The global commercial production of acetylated wood accounts for 120,000 $m^3$/year, and it is mainly concentrated on radiata pine [10]. The process improves dimensional stability and UV resistance and reduces surface erosion by 50%. All those factors are very relevant, especially while using wood as a façade material [11]. The UV protection is most effective at higher weight gain (over 20%) when the substitution of cellulosic hydroxyl groups occurs [12]. It is because cellulose derivatives are generally less susceptible to photodegradation than unmodified cellulose [13]. The durability and dimensional stability of acetylated wood are substantially improved while the mechanical strength remains similar to untreated wood [7,14–16]. The acetylated wood, same as natural wood, is susceptible to weathering in outdoor conditions. After initial stability against UV radiation, it begins to fade and becomes grey like other wood species. As the weathering progresses, the deacetylation of the wood surfaces occurs in addition to the dilute acids, which could increase the degradation of wood [12]. Acetylated wood is also susceptible to mould and blue stain fungi since no toxic chemicals are added to the wood [17]. A compressive review of how the modification of wood affects the resistance of wood to weathering was provided by Jirouš-Rajković et al. [17]. Reported papers show both positive and negative effects of the acetylation process to weathering extent. Variations in wood performance were also noticed when performing laboratory and field tests. The acetylation process can be enhanced by merging it with additional processes, such as the application of surface treatment [15]. Due to improved dimensional stability and resistance against fungal decay, acetylated wood has shown positive effects on the performance of coatings [18–20]. Even if several studies reported the performance of acetylated wood, both the unprotected and coated alteration of material properties at different levels—macro, micro, and molecular—is important for understanding the drawbacks of the process and its further improvement, especially while considering alternative wood species [21,22]. Most of the reported work is related to acetylated softwood or hardwood acetylated in laboratory conditions [17]. The rising emphasis on semi-natural forest management, which favours hardwoods, along with climate change is leading to a rapid increase in the proportion of broad-leaved trees (generally referred to as hardwoods) within forest stocks. A significant portion of harvested hardwoods is currently used as fuel wood rather than being allocated to appropriate utilisation paths. Therefore, new and improved strategies for competitive hardwood utilisation should be developed based on research findings on hardwoods.

To enhance research on acetylated wood, particularly moving beyond the predominant focus on acetylated softwoods and laboratory conditions, several strategies should be adopted. First, it is essential to study a broader range of wood types. This includes

expanding research to encompass more varieties of hardwoods and softwoods [17]. Additionally, conducting experiments under realistic environmental conditions, rather than solely in controlled laboratory settings, will provide more applicable results. This could involve simulating outdoor conditions with varying humidity, temperature fluctuations, and exposure to natural elements, such as UV radiation and biological organisms. Long-term studies are also crucial. Performing extended durability and aging studies will help assess the effectiveness of acetylation over several years [16]. Monitoring the performance of acetylated wood in real-world applications, such as in construction or outdoor installations, will yield valuable insights into its long-term viability and maintenance requirements [15]. Comparative studies should be conducted to evaluate the effectiveness of acetylation relative to other wood treatment methods, such as heat treatment or chemical preservatives. Understanding how different species of wood react to acetylation and why some perform better than others will provide a more comprehensive understanding of the process. Enhanced testing methods can significantly improve the quality of research. Utilising advanced analytical techniques, such as scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), or infrared microscopy, will allow for a detailed chemical and structural analysis of acetylated wood. Additionally, assessing the mechanical and physical properties, such as strength and hardness, post-acetylation will provide a complete picture of its benefits and limitations [15]. Environmental and health impacts must also be considered. Conducting sustainability assessments and life cycle analyses will help understand the broader environmental implications of the acetylation process [5]. Investigating the potential health effects of using acetylated wood, particularly in indoor environments, is equally important. Collaboration with industry stakeholders is vital for practical applications. By testing acetylated wood in commercial and residential settings, researchers can gather real-world data and insights. Developing and contributing to industry standards and guidelines will help ensure the safe and effective use of acetylated wood [22]. Implementing these strategies will significantly enhance the understanding of acetylated wood, highlighting its benefits, limitations, and real-world applications. The goal of this study is to comprehensively evaluate the natural weathering performance of three wood species, alder, beech, and radiata pine, modified with an acetylation process in industrial conditions to potentially expand the utilisation of hardwood species in the wood sector.

## 2. Materials and Methods

### 2.1. Experimental Samples

Acetylated wooden boards with a 20% acetyl weight gain on average, manufactured from two varieties of hardwood, black alder (*Alnus glutinosa* L.) #1, European beech (*Fagus sylvatica* L.) #2, and softwood represented by radiata pine (*Pinus radiata* D. Don) #3, were used as experimental samples. Fifty-four small blocks (150 L × 75 W × 20 T $mm^3$, respectively) were cut out from each of the 3 sample types for 6 natural weathering periods and 3 replicas for each test. The wood modification was performed at the commercial production facilities of Accsys Technologies in the Netherlands. The edges of the samples were sealed with SA10 clear, water-based, one-component sealer to avoid water uptake from the unexposed side.

### 2.2. Weathering Tests

Natural weathering tests were performed in San Michele, Italy (46°11′15″ N, 11°08′00″ E). Samples were mounted on vertical stands oriented to the south, simulating a building façade. The meteorological data captured during the tests are presented in Table 1. The duration of the weathering experiment was 15 months, starting in March 2017. Every third month, three replicas were collected resulting with the collection of samples exposed to 0, 3, 6, 9, 12, and 15 months. Samples were stored in a climatic chamber (20 °C, 65% RH) before further measurements.

**Table 1.** Weather data acquired during weathering.

| Exposure Month | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean temp (°C) | 12 | 14 | 19 | 24 | 25 | 25 | 17 | 14 | 7 | 1 | 4 | 4 | 17 | 19 | 24 |
| Total rain (mm) | 32 | 108 | 50 | 36 | 27 | 17 | 6 | 1 | 28 | 3 | 1 | 7 | 4 | 15 | 5 |
| Days of rain | 8 | 11 | 15 | 10 | 10 | 14 | 3 | 6 | 4 | 4 | 3 | 11 | 11 | 21 | 12 |
| RH (%) | 49 | 45 | 51 | 51 | 50 | 52 | 68 | 62 | 69 | 74 | 82 | 55 | 55 | 67 | 49 |
| Mean wind (km/h) | 7 | 9 | 7 | 9 | 8 | 6 | 5 | 5 | 4 | 3 | 3 | 5 | 6 | 6 | 8 |

### *2.3. Characterisation Methods*

#### 2.3.1. Digitalisation

All experimental samples were digitalised with an office scanner HP Scanjet 2710, HP Milan, Italy (300 dpi, 24 bit) and saved as TIF files.

#### 2.3.2. Colour Measurement

Colour variations were evaluated using a spectrometer based on the CIE L*a*b* system, which defines colour through three parameters: L* (lightness), a* (red-green), and b* (yellow-blue). Measurements of the CIE L*a*b* colours were taken with a MicroFlash 200D spectrophotometer (DataColor Int., Lawrenceville, GA, USA). The illuminant used was D65, and the viewing angle was set to 10°. Each sample was measured at five randomly chosen spots. Visible defects, such as cracks or knots, were intentionally omitted. The mean values were taken as the representative colour, while the highest and lowest readings were noted to assess the natural variation in colour distribution. ANOVA was used to determine the effects of weathering on the colour values (L*, a*, b*) of investigated wood specimens at the 95% confidence level.

#### 2.3.3. Gloss

The surface gloss was measured by a gloss meter REFO 60 (Dr. Lange, Düsseldorf, Germany) with incidence and reflectance angles of 60°. To accurately capture the optical heterogeneity of light reflectance from the wood surface, measurements along and across the fibre direction were taken ten times on each specimen. ANOVA was used to determine the effects of weathering on the gloss values of investigated wood specimens at the 95% confidence level.

#### 2.3.4. Microscopic Observation and 3D Roughness Measurement

Microscopic observations and 3D surface topography scanning were performed with a digital microscope Keyence VHX-6000 (Keyence, Osaka, Japan) according to procedure described by authors [20]. The surface roughness quantifiers' arithmetical mean height (*Sa*), skewness (*Ssk*), and kurtosis (*Skt*) were calculated with proprietary Keyence software VHX-6000 3.2.0.121.

#### 2.3.5. Contact Angle and Surface Free Energy

Optical tensiometer Attention Theta Flex Auto 4 (Biolin Scientific, Gothenburg, Sweden) was used for dynamic contact angle measurements. Five replicates of a sequence with distilled water and formamide were run on each sample using the sessile drop method. The drop volume of 4 µL was controlled with a precise dispenser, and measurement lasted for 20 s. Contact angle for both investigated liquids was calculated using Laplace equation, while the surface free energy was computed following OWRK/Fowkes method [23]. For all investigated samples, the total surface free energy ($\gamma^{tot}$) as well as its polar ($\gamma^{p}$) and disperse ($\gamma^{d}$) components were determined.

#### 2.3.6. Infrared Measurement

Alpha II spectrophotometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a diamond crystal was used for the infrared measurements. Spectra were recorded on

attenuated total reflectance mode from an average of 64 scans in the range of 4000–400 $cm^{-1}$ at resolution of 4 $cm^{-1}$. Three measurements were performed on each sample. The PLS_Toolbox (Eigenvector Inc., Manson, WA, USA), available as an extension of the Matlab package (Mathworks, Natick, MA, USA), was used for processing and analysing the spectra, including extended multiplicative scatter correction (EMSC) as well as principal component analysis (PCA) for averaging. The pre-processing included atmospheric compensation and EMSC followed by averaging three spectra measured on each sample. Spectra were smoothed (11 points), and 1st order baseline was applied. The list of peaks is summarised in Table 2.

**Table 2.** Band assignment for FT-IR transmittance spectra [24–27].

| Band Number | Peak Position ($cm^{-1}$) | IR Band Assignment |
|---|---|---|
| 1 | 985 | CO valence vibrations |
| 2 | 1024 | CO stretching in cellulose and non-cellulose polysaccharides |
| 3 | 1060 | C–O + C–C stretch of cellulose |
| 4 | 1110 | Aromatic skeletal; C–C stretch |
| 5 | 1160 | CO stretching in ester groups in lignin |
| 6 | 1201 | untreated cellulose (ρ OH; δ CH) |
| 7 | 1240 | antisymmetric C–O stretching vibration |
| 8 | 1265 | guaiacyl ring vibrations and CO stretching lignin, C–C and C–O stretching |
| 9 | 1320 | C–H vibration in cellulose; C–O in syringil and condensed guaiacyl units |
| 10 | 1334 | vibration in CH and stretching in CO related to syringil ring |
| 11 | 1370 | C–H deformation vibrations of the $CH_3$ group |
| 12 | 1425 | vibration of aromatic structures in lignin |
| 13 | 1452 | aromatic skeletal vibrations of lignin and CH2 vibration in cellulose |
| 14 | 1508 | aromatic skeletal vibrations of lignin and C=O stretching |
| 15 | 1592 | conjugated carbonyl C=O stretching |
| 16 | 1650 | absorbed water (hydrogen-bonded), conjugated carbonyls –C=C–C=O |
| 17 | 1740 | non-conjugated carbonyl C=O stretching, molecular vibrations of acetyl C=O groups |
| 18 | 2890 | C-H stretching in methyl and methylene groups |
| 19 | 2940 | asymmetric stretching vibrations of CH related to methyl and methylene in lignin, cellulose and hemicellulose |
| 20 | 3149 | -OH stretching in cellulose |
| 21 | 3280 | C-H stretching in methyl and methylene groups |
| 22 | 3340 | -O(3)H O(5) intramolecular hydrogen bonds in cellulose |
| 23 | 3460 | moderately H-bonded water |
| 24 | 3565 | valence vibration of H bonded OH groups |
| 25 | 3602 | weakly H-bonded water |

#### 2.3.7. Thermogravimetric Analysis

Thermogravimetric analyses were performed using the thermogravimetric analyser Discovery TGA-5500 (Waters TA Instruments, New Castle, DE, USA). A high-resolution dynamic method with a heating rate of 50 °C $min^{-1}$, a final temperature of 800 °C, a resolution of 4, and a sensitivity value of 1 was used for all samples. For each analysis, 5–10 mg of the wooden surface was used as reference, and samples were weathered for 15 months. Three samples from each wood species were analysed. The electro-balance was purged with nitrogen at a flow rate of 10 mL/min and the furnace with a flow rate of 25 mL/min. Thermogravimetric (TG) and derivative thermogravimetric (DTG) data generated with instruments were decoded using TA Instruments TRIOS software v5.3.0.48151, New Castle, DE, USA.

## 3. Results and Discussion

### *3.1. Appearance Changes*

The alteration in appearance due to natural weathering is presented in Figure 1. The lightening after three months of exposure was noticed for all three acetylated wood

species. The colour was maintained for the following three months. The photo bleaching of acetylated wood is mainly caused by visible light [28]. During the progression of the weathering process, acetylated wood and other wood-based products turned to grey tonality [29]. The presence of mould was noticed in the 9th month due to favourable outdoor conditions [23,30]. The area of mould progressively expands during the weathering. The overall tonality at month 15 was grey. A similar phenomenon caused by the biotic attack resulting in grey-blue or green spots on the surface of the material has been previously reported [31,32]. This process might be desired under certain circumstances when rapid homogenisation within the local context is intended [33]. However, in most cases, the visual changes and uneven discoloration on the wooden claddings are negatively perceived [34].

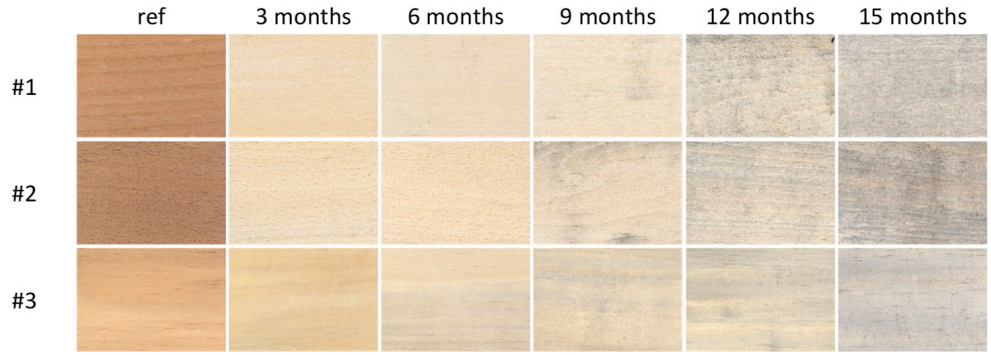


**Figure 1.** Appearance of experimental samples exposed to natural weathering. Note: #1 black alder, #2 European beech, #3 radiata pine.

The wood acetylation researched in this study leads to the reduction in hydroxyl groups, which are primary functional groups that interact with the moisture in wood and, consequently, minimise the shrinkage/swelling [11]. All samples exhibit only a slight disintegration of the surface, evidenced by small cracks or raised fibres.

Figure 2 presents the colour changes of the experimental samples. The three investigated species, acetylated alder (#1), acetylated beech (#2), and acetylated radiata pine (#3), revealed tendencies towards a rapid change in colour during the initial weathering period.

However, a similar pattern of the CIE L*a*b* alteration observed in the investigated acetylated hardwoods (alder and beech) contrasted with acetylated radiata pine. The lightness parameter (CIE L*) measured for the acetylated pine was relatively stable, with a minor increase at the initial phase of the weathering. CIE a* gradually declined for all samples. From the 6th month of exposure, the values were stable in all three cases. Values of CIE b* gradually dropped after a slight gradual increase at the beginning of the test.

A single-factor ANOVA was conducted to determine the effect of weathering on the colour measurement of wood. The colour parameters (L*, a*, and b*) were recorded for different weathered wood samples to see if weathering had a significant impact on the gloss. The ANOVA was performed to compare the colour measurements among the six different groups (reference and weather for 3, 6, 9, 12, and 15 months). The results indicated that there was no statistically significant difference in gloss measurements between the groups. The values were as follows: L* #1 $F(2, 51) = 0.17$ ($p = 0.84$), #2 $F(2, 51) = 0.39$ ($p = 0.67$), and #3 $F(2, 51) = 2.54$ ($p = 0.08$); a* #1 $F(2, 51) = 0.09$ ($p = 0.91$), #2 $F(2, 51) = 0.23$ ($p = 0.79$), and #3 $F(2, 51) = 0.42$ ($p = 0.66$); and b* #1 $F(2, 51) = 0.39$ ($p = 0.67$), #2 $F(2, 51) = 0.68$ ($p = 0.51$), and #3 $F(2, 51) = 0.81$ ($p = 0.45$). The ANOVA results suggest that the weathering duration did not have a significant effect on the colour measurement of the wood samples. The mean colour values for the wood samples weathered for different durations were not significantly different from each other, indicating that weathering, under the conditions tested, did not substantially alter the wood appearance.

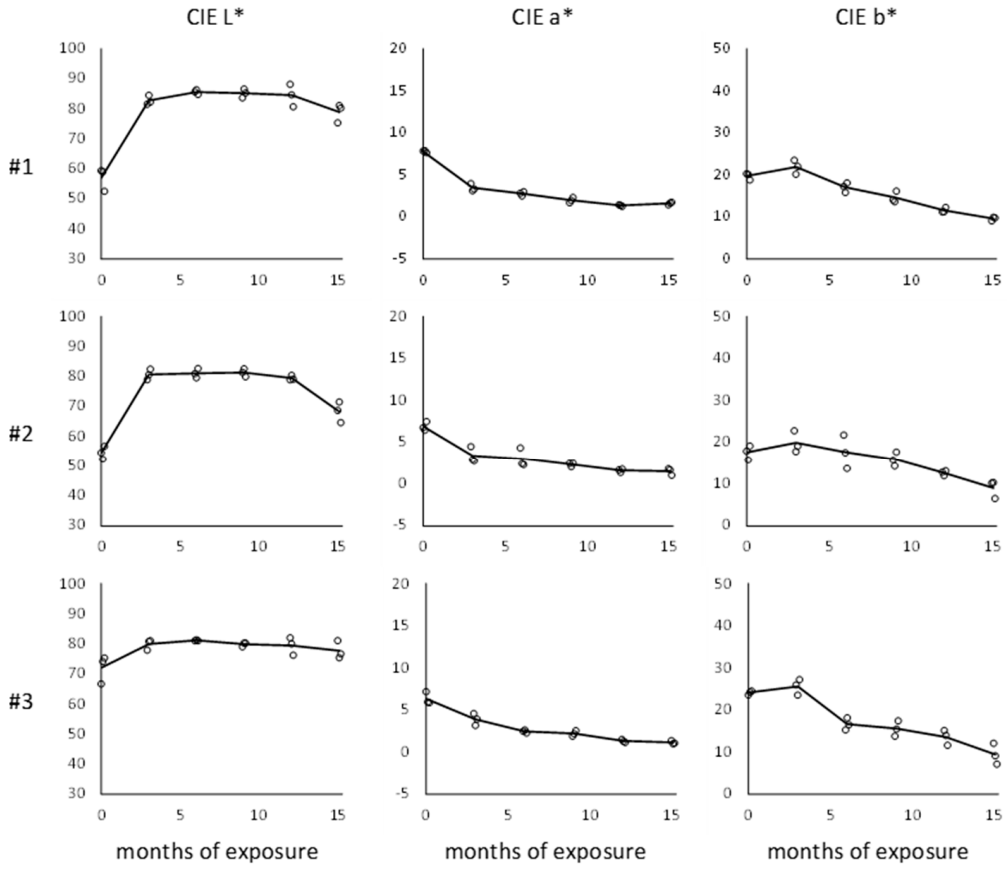


**Figure 2.** *CIE L*, a**, and *b** coordinates of acetylated wood samples exposed to natural weathering. Note: #1 black alder, #2 European beech, #3 radiata pine.

The results of the gloss measurement are presented in Figure 3. The values were relatively constant for all three acetylated wood species during the whole weathering period. A loss of gloss is an indicator of degradation at the early stage as a result of physical changes, such as rising fibres, cracking, checking, or the chemical photodegradation of wood chemical components [35,36].

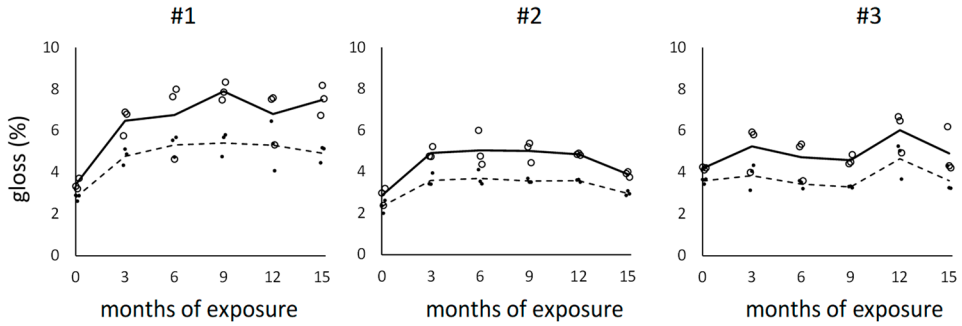


**Figure 3.** Gloss changes of acetylated wood samples exposed to natural weathering (note: circle and solid line—gloss along fibres, dots and dash line—gloss perpendicular to fibres). Note: #1 black alder, #2 European beech, #3 radiata pine.

A single-factor ANOVA was conducted to determine the effect of weathering on the gloss measurement of wood. The gloss measurements (along and perpendicular to fibres) were recorded for different weathered wood samples to see if weathering had a significant impact on the gloss. The ANOVA was performed to compare the gloss measurements among the six different groups (reference and weather for 3, 6, 9, 12, and 15 months). The

results indicated that there was no statistically significant difference in gloss measurements between the groups. The values were as follows: gloss along #1 $F(4, 85) = 0.21$, $p = 0.92$; #2 $F(4, 85) = 1.04$, $p = 0.99$; and #3 $F(4, 85) = 0.53$, $p = 0.71$ and gloss perpendicular #1 $F(4, 85) = 0.12$, $p = 0.97$; #2 $F(4, 85) = 0.07$, $p = 0.98$; and #3 $F(4, 85) = 0.14$, $p = 0.97$. The ANOVA results suggest that the weathering duration did not have a significant effect on the gloss measurement of the wood samples. The mean gloss values for the wood samples weathered for different durations were not significantly different from each other, indicating that weathering, under the conditions tested, did not substantially alter the glossiness of the wood.

The initial exposure to UV light results in the rapid degradation and depletion of the lignin on the wood surface. Once most of the easily degradable lignin is broken down and removed, the remaining wood structure consists mostly of cellulose and hemicellulose, which are less susceptible to further photodegradation [28]. Moreover, the degradation products from lignin and other wood components can sometimes form a thin, protective layer on the wood surface. This layer may absorb some of the UV light and protect the underlying wood from further rapid degradation [28]. The initial oxidative reactions that cause bleaching also tend to stabilise the wood's surface. The newly formed compounds from these reactions can be more resistant to further oxidation, leading to a slower rate of colour change. Once the initial leaching of coloured extractives (such as tannins and other pigments) occurs, the amount of these compounds remaining in the wood is significantly reduced. Over time, the surface of the wood reaches a weathering equilibrium [1]. The initial rapid changes slow down as the wood surface becomes more uniformly weathered and acclimated to its environment. The ongoing weathering processes occur at a much slower, more uniform rate, resulting in a more stable colour. All those processes lead to the degradation and removal of the most reactive and colour-changing components of the wood at the initial stage of the weathering process. Once these components are depleted or stabilised, the wood's colour becomes more uniform and stable, resulting in less noticeable changes over time [12,28].

### 3.2. Surface Topography

An increase in the surface roughness was observed in all three of the investigated acetylated wood species. The results for samples #1, #2, and #3 are presented in Figure 4, Figure 5, and Figure 6, respectively. The progress of surface erosion is reflected in the surface profile presented at the bottom of each figure. It is confirmed by the surface roughness parameters presented below the images.

Parameters such as arithmetical mean surface height (*Sa*) or the arithmetical mean height of the roughness profile (*Ra*) are the basic irregularity quantifiers for the two-dimensional surface roughness profiles. For both hardwoods, the values of *Sa* increased steadily. However, it remained moderately constant for acetylated radiata pine. For hardwoods, the increase in Sa suggests a rougher surface as erosion progresses, potentially influencing dirt and spore accumulation. For radiata pine, the constant Sa indicates stability in surface roughness despite exposure to erosive elements, which may affect how dirt and spores accumulate differently compared to hardwoods. The decrease of skewness (*Ssk*) observed for all species is associated with the loss of fibres and the general progress of surface erosion. Kurtosis (*Skt*) is an indicator of the sharpness of the topography histogram profile. Values of *Skt* greater than three signify a leptokurtic distribution, characterised by fatter tails than those of normal/Gaussian distributed ones [20]. The spiked appearance of the surface irregularity histogram is due to the planning process used to create the flat samples by the industrial partner. The observed changes in *Skt* suggest a shift towards a platykurtic distribution, reflecting a more balanced representation of surface peaks and valleys. It should be noted that even if the mechanism of the surface roughness alterations in the case of both acetylated hardwood specimens was clearly interpretable, it was not possible to observe the same trends in the acetylated radiata pine (softwood) samples. In

general, an increase in the surface roughness during weathering is associated with the erosion of the wood surface that occurs gradually along the weathering progress [1].

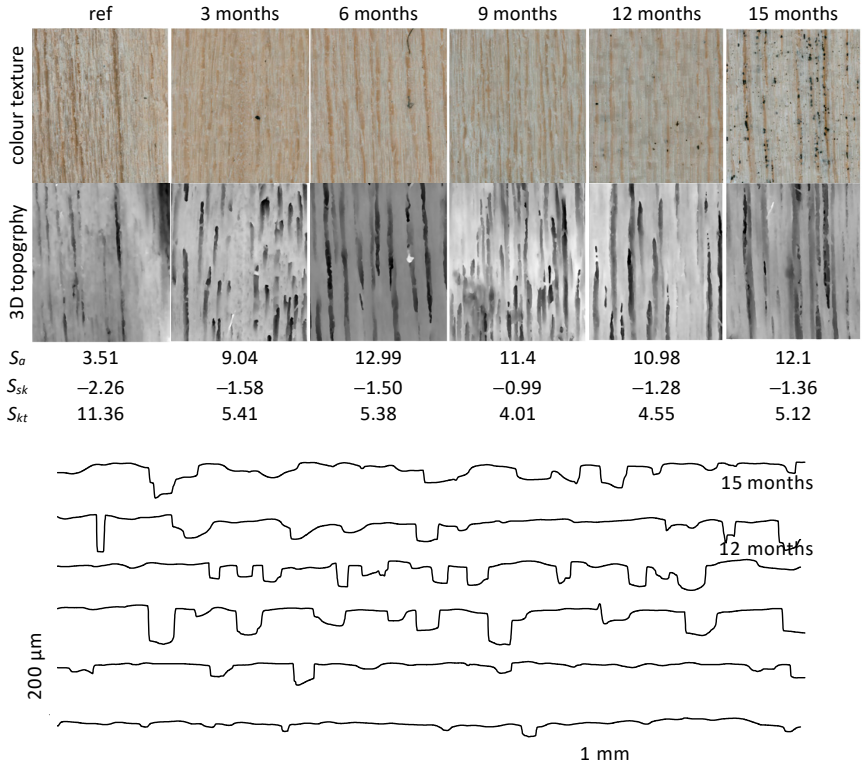


**Figure 4.** The 3D surface topography map, typical surface profiles, and high magnification images of the acetylated alder wood (sample #1) exposed to 15 months of natural weathering.

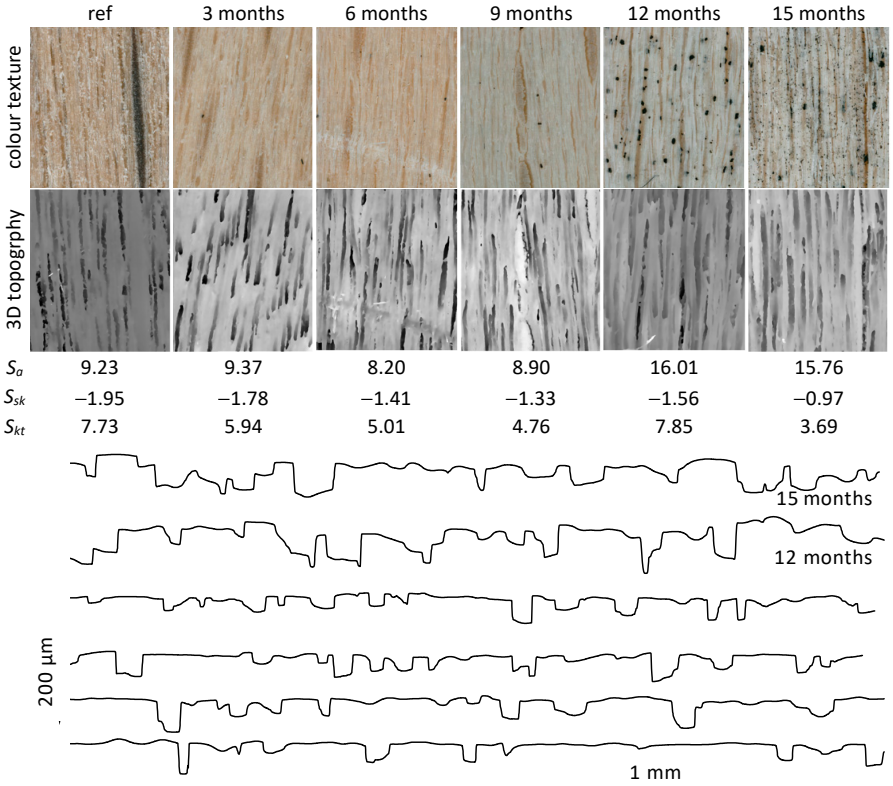


**Figure 5.** The 3D surface topography map, typical surface profiles, and high magnification images of the acetylated beech wood (sample #2) exposed to 15 months of natural weathering.

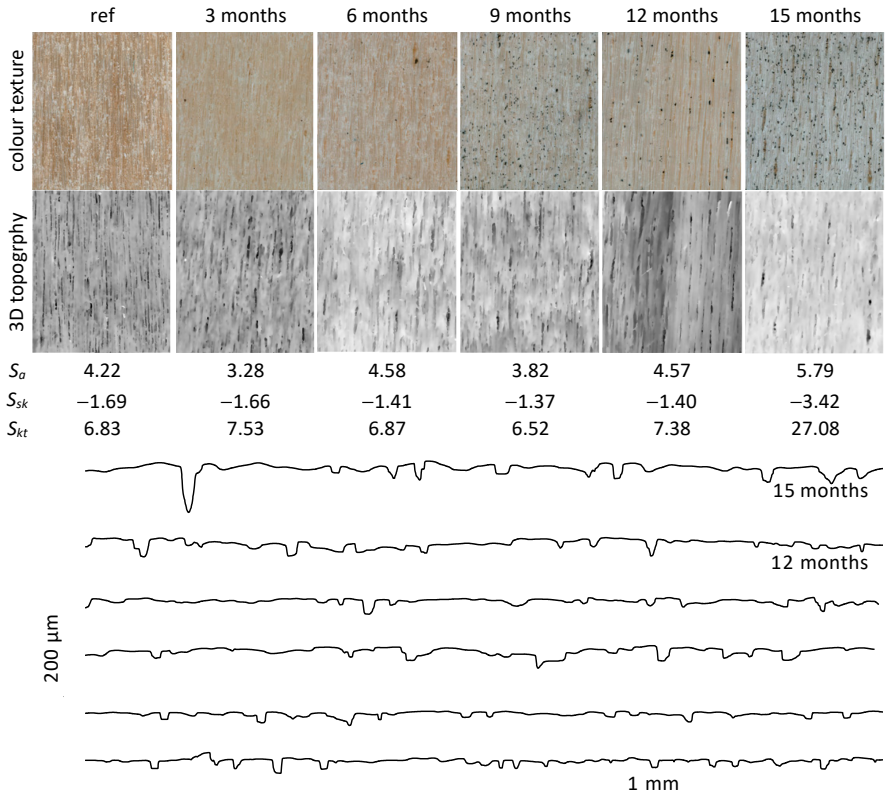


**Figure 6.** The 3D surface topography map, typical surface profiles, and high magnification images of the acetylated radiata pine wood (sample #3) exposed to 15 months of natural weathering.

Changes in the surface roughness due to weathering are also linked with the accumulation of dirt and spore attachment and germination [32]. Rougher surfaces tend to accumulate more dirt and spores due to increased surface area and more pronounced peaks and valleys that can trap particles. Spores visible at the high magnification colour images were also observed on the macro-scale images presented in Figure 1. The surface most affected by mould was that of acetylated beech (sample #2) even though the acetylation process improves the overall mould resistance of wood [37,38]. The study highlights that for hardwoods, increased surface roughness is linked with higher erosion and potentially greater dirt/spore accumulation. In contrast, radiata pine shows constant roughness, suggesting different interactions with environmental factors. However, the detailed interactions between surface roughness parameters, erosion, and dirt/spore accumulation remain unexplored and warrant further investigation.

### *3.3. Wettability of Wood Surface*

Figure 7 presents the result of the dynamic contact angle measurement with water and formamide. The contact angle (θ) measured with water was higher than that with formamide for all investigated cases. A low θ value was observed for all acetylated wood species after the weathering process, signifying easy spreads of liquids over the assessed surface. In the acetylated hardwoods (#1 and #2), the drop in θ value was observed after three months, followed by rather similar values (from month 3 to month 15). In acetylated radiata pine wood, the θ values gradually lowered over a period of up to six months, then they plateaued, with a slight oscillation around 15°.

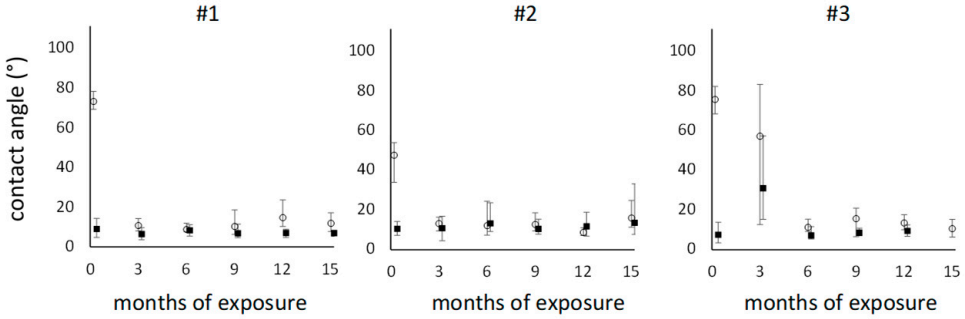


**Figure 7.** Contact angle measured after 3 s of wetting with water (white circle) and formamide (black square). Note: #1 black alder, #2 European beech, #3 radiata pine.

The high data variation in the contact angle measurements of weathered wood noticed in the case of radiata pine exposed for three months might be due to a combination of factors related to the wood's surface roughness, chemical heterogeneity, biological activity, measurement technique variability, surface contaminants, and the inherent properties of the wood species and grain orientation. These factors contribute to the complexity and variability of contact angle measurements on weathered wood surfaces. Weathered wood often develops a rougher surface texture due to the erosion of softer wood components and the exposure of harder fibres. This increased roughness can lead to variations in contact angle measurements because the water droplet may interact differently with uneven surfaces. Moreover, the weathering processes, such as UV degradation and oxidation, do not occur uniformly across the wood surface. This results in chemical heterogeneity, where some areas might be more degraded than others. The presence of varying degrees of lignin degradation, extractive loss, and oxidation can cause inconsistent contact angles.

The contact angle measurement implies the wettability with water (or other liquids) of the exposed material surface. The extent to which the θ changes is an important indicator of the progression of weathering [39]. The contact angle measurement allows for the estimation of the surface free energy (SFE). This can be calculated using the θ data by combining at least two wetting liquids with different physical and chemical properties. The SFE was determined following the OWRK/Fowkes energy theory [40]. The SFE results for all measured samples are presented in Figure 8. The values of the SFE for all three acetylated species oscillated around 70 mJ·m$^{-2}$. The values of $\gamma^p$ were rather constant for all investigated species. In the case of $\gamma^d$, the drop occurred after 3 months of oscillating around 15 mJ·m$^{-2}$. A slightly different behaviour was observed in radiata pine, the only softwood species. The weathering process of unprotected wood enhances wettability due to the degradation of lignin and leaching of the extractives from the surface [41,42].

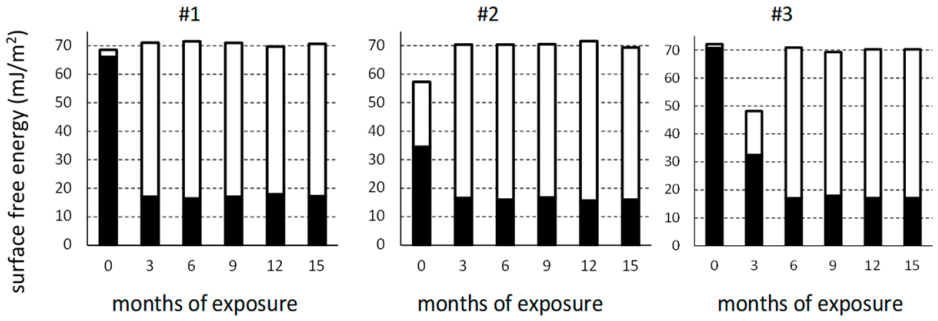


**Figure 8.** Surface free energy ($\gamma^{tot}$), including polar ($\gamma^p$) (white) and disperse ($\gamma^d$) (black) components. Note: #1 black alder, #2 European beech, #3 radiata pine.

### *3.4. Chemical Changes in Wood Surface*

FT-IR spectra measured in attenuated total reflectance mode on samples before and after weathering reflect the progress of changes related to the functional groups of wood

polymers. The interpretation based on the band assignment is presented in Table 1. The most evident are changes in the spectra intensity of bands #2, #7, and #17, assigned to cellulose and non-cellulose polysaccharides, antisymmetric C–O stretching vibration, and non-conjugated carbonyl C=O stretching, respectively. At 1740 $cm^{-1}$ (band #17), changes in the vibrations related to acetyl C=O groups as a result of the acetylation process are observed [43]. The C–H deformation vibrations of the methoxy group at 1370 $cm^{-1}$ do not differ in intensity. A clear shift of band #7 associated with anti-symmetric C–O stretching vibration (C–O–C=O) toward a higher wavenumber can be seen in all weathered samples. Bands #9 and #16 are especially evident in the acetylated radiata pine, showing more advanced changes as compared to both hardwood species. They correspond to C–H vibration in cellulose, C–O in syringyl derivatives/condensed guaiacyl units, and hydrogen-bonded absorbed water. Some authors suggest that an increase in absorbance around the wavenumber of 1650 $cm^{-1}$ is related to aldehyde and ketone groups on C 2 and C 3 of the pyran or furan units [44]. It was reported that the formation of a carbonyl group chromophore increases the intensity of the C = O band at 1650 $cm^{-1}$ [45,46]. The region 3900–2700 $cm^{-1}$ reflects essentially the amount and structure of hydroxyl groups in various types of hydrogen bonding of wood components [24]. Although bands assigned to hydroxyl groups in the IR spectrum become better resolved after deconvolution, the changes observed in samples #20, #22, and #23 indicate alterations in the hygroscopic properties of wood exposed to the weathering [41]. The intensity of peaks #7 and #14 related to lignin diminishes as the weathering progresses. In the case of band #14, the peaks disappear, indicating lignin decomposition on the wood surface. Similar chemical behaviour on spruce after 168 h of UV irradiation has been previously reported [47]. Consequently, the degradation of lignin evidenced by IR spectra resulted in a more hydrophilic surface, presented in Figure 9.

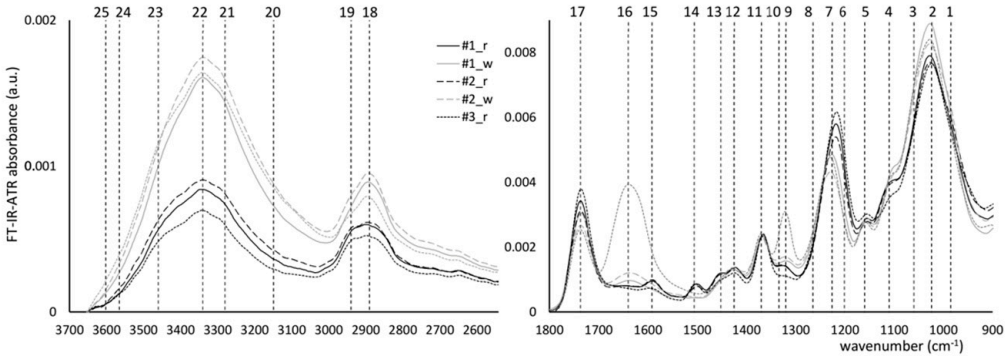


**Figure 9.** Changes to FT-IR attenuated total reflectance spectra of investigated acetylated samples before (r) and after 15 months of natural weathering (w). Note: #1 black alder, #2 European beech, #3 radiata pine.

The different mechanisms of degradation for investigated species due to the weathering process can be observed in Figure 10, where the PCA results are presented. The upper part of Figure 10a presents the score distribution. PC1 explains over 80% of the variance divide in the analysed samples to the reference (left side of the figure) and after weathering (right side). Moreover, the weathered samples of acetylated softwood (radiata pine) are located far from other acetylated hardwood (alder and beech), meaning different kinetics and/or the intensity of degradation is most likely related to wood type. PC2 versus PC3 demonstrates that weathered hardwood is separated from the rest of the samples. The limitation here is a two-dimensional presentation of the scores; therefore, the scores of weathered acetylated radiata pine, even if not very evident as different, occupy a different space (visible in the figure on the left—PC1 versus PC2). The interpretation of loadings presented in Figure 10b provides insight into which bands differ in the investigated wood species. Positive loadings signify a positive correlation between a variable and a principal component, meaning an increase in one leads to an increase in the other. Conversely,

negative loadings indicate a negative correlation. Large loadings, whether positive or negative, suggest that a variable has a strong influence on that principal component. PC1 explains a majority (over 80%) of variance and exhibits positive loadings in bands #3, #9, #16, #18, #20, #21, #22, and #23. Negative loadings appear for bands #6 and #17. Part of the PC1 loading in the region 3900–2700 $cm^{-1}$ corresponds to IR spectra presented in Figure 9. Several bands related to various wood chemical components as well as bonded water pronounced in the first loading signify that the chemical changes occurred due to the weathering process [24]. PC2 and PC3 explain less variance, 12% and 4%, respectively; however, they also highlight bands that were noticeable in the IR spectrum.

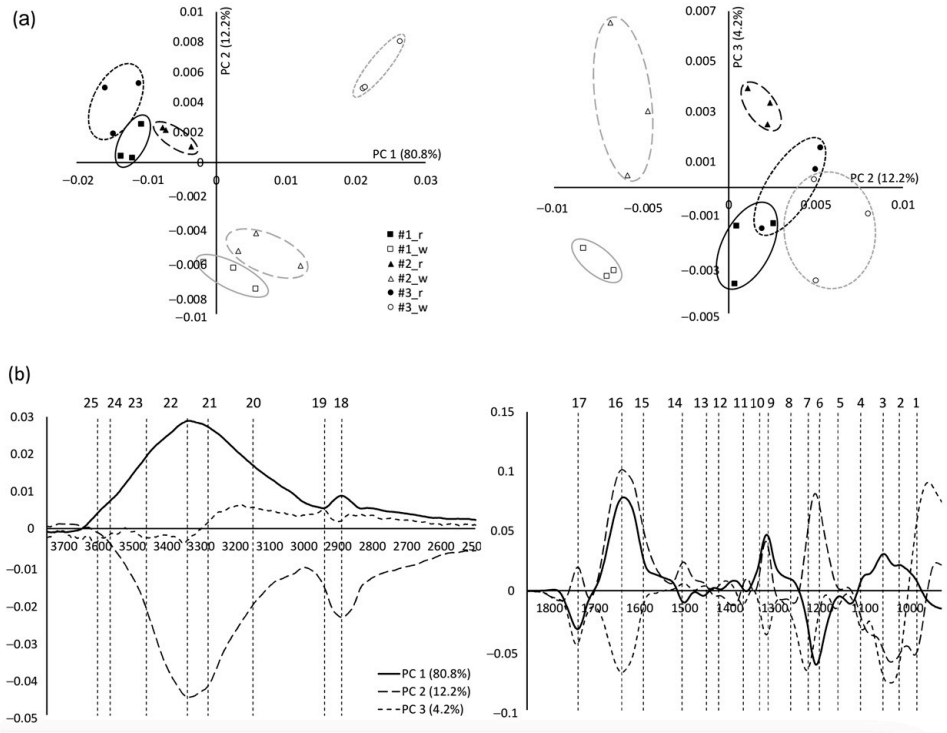


**Figure 10.** Principal component analysis (PCA) of FT-IR attenuated total reflectance spectra of investigated acetylated samples before (r) and after 15 months of natural weathering (w); (**a**) scores and (**b**) loadings. Note: #1 black alder, #2 European beech, #3 radiata pine.

Even though the acetylation process significantly enhances the wood's overall durability and stability, the bleaching of acetylated wood during natural weathering is primarily due to the breakdown of lignin by UV light, oxidation processes, and the leaching of coloured compounds. Ultraviolet (UV) light from the sun breaks down lignin in the wood, even in acetylated wood. Lignin degradation leads to the formation of chromophoric groups, which cause the wood to change colour, often resulting in the bleaching or greying of the wood surface [12,28]. Exposure to oxygen leads to the oxidative degradation of wood components, especially on the surface. This oxidation can break down lignin and hemicelluloses, leading to further colour changes and the potential weakening of the wood's surface. Acetylated wood is more resistant to hydrolysis due to the reduced availability of hydroxyl groups. However, prolonged exposure to moisture can still cause some degree of hydrolysis, particularly if the acetylation is not uniform or if the wood is damaged.

### *3.5. Thermal Properties of Weathered Wood*

The thermogravimetric (TG) and 1st derivative thermogravimetric (DTG) curves obtained for the acetylated wood samples before and after 15 months of weathering are presented in Figure 11. In addition, thermal parameters related to the degradation of the surface of the samples are reported in Table 3. The thermal analysis showed clear

differences between weathered and non-weathered acetylated surfaces. The shift of the DTG maxima to lower temperatures is related to the decrease in the stability of wood by increasing the time of exposure to the natural weathering process. The acetylated hardwood samples showed higher thermal stability than acetylated radiata pine (reflected by $T_{5\%}$ and $T_{max}$) with a maximum rate of weight loss around 353 °C for acetylated alder and beech and 347 °C for acetylated pine. The sharp decrease in weight during this degradation step is due to the splitting of cellulose macromolecules. The acetylated samples showed a small degradation step also at 310–330 °C (especially appreciable in #2 as a peak), followed by the main degradation step. This degradation is less intense in the weathered samples and totally undetectable in #2. The degradation at this temperature is usually related to the decomposition of the hemicelluloses (observed also in FT-IR spectra) and the slow degradation of lignin [48,49]. Acetylated radiata pine has a higher char residue at 800 °C than the acetylated hardwood samples (17% vs. 12%). The initial degradation temperature corresponding to 5% weight loss (T5%) is marked lower for weathered wooden surfaces, as can be observed in Table 3. The main degradation step of the weathered wooden samples is also lower in the case of #1 (alder); however, no considerable decrease was observed for #2 (beech) and #3 (radiata pine). Char residue was also lower in the case of all weathered samples. The difference between the reference and weathered wood was 3.7, 0.4, and 7.4 for #1, #2, and #3, respectively, signifying the lowest residue content for beech and the highest for radiata pine. According to Slopiecka [50], the residue consists primarily of charcoal from lignin decomposition. The lower char content in weathered wood is because of the lower lignin content on the wooden surface as a result of the degradation due to the weathering process [51].

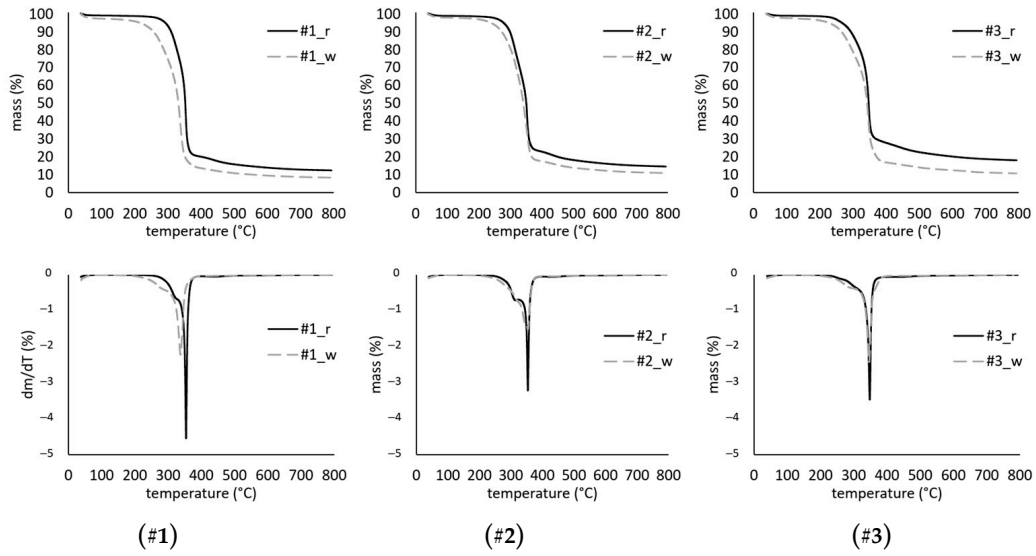


**Figure 11.** The thermogravimetric (TG) and 1st derivative thermogravimetric (DTG) curves obtained for the acetylated wood samples before (r) and after weathering (w). Note: (#1) black alder, (#2) European beech, (#3) radiata pine.

**Table 3.** Thermogravimetric parameters of investigated samples.

| Parameters | #1r | #1w | #2r | #2w | #3r | #3w |
|---|---|---|---|---|---|---|
| $T_{5\%}$ | 292.4 | 219.1 | 278.8 | 241.9 | 276.4 | 230.5 |
| $T_{50\%}$ | 352.4 | 331.9 | 350.6 | 341.2 | 347.4 | 342.7 |
| $T_{max}$ | 353.9 | 337.2 | 353.6 | 353.3 | 347.9 | 345.8 |
| Residue | 12.1 | 8.4 | 12.2 | 11.8 | 17.9 | 10.5 |

### 3.6. Practical Application of Conducted Research

Experiments on naturally weathered acetylated wood provide valuable insights that can significantly impact its practical applications in several ways. Findings from natural weathering experiments can identify potential areas for improvement in the acetylation process or in additional treatments to enhance performance. Manufacturers can develop new or improved acetylation processes and compatible protective coatings, leading to better-performing wood products that meet market needs more effectively. Understanding the durability of acetylated wood under natural weathering conditions helps quantify its resistance to decay, moisture, and UV damage. This information allows architects, builders, and manufacturers to confidently use acetylated wood in outdoor applications, where longevity is critical, such as decking, siding, and outdoor furniture [52]. Findings on how acetylated wood weathers over time can indicate the frequency and type of maintenance required to preserve its appearance and structural integrity [53]. Homeowners and facility managers can develop better maintenance schedules, ensuring the wood remains aesthetically pleasing and functional for longer periods, reducing long-term costs. Data from weathering experiments can be used to create models predicting the performance of acetylated wood over time under various environmental conditions. Such models facilitate informed decisions about the suitability of acetylated wood for specific climates and exposure conditions, aiding in material selection and risk management [54]. Natural weathering studies reveal how acetylated wood's colour and texture change over time, which is crucial for aesthetic planning. In this case, designers and architects can anticipate changes in appearance and plan for them, either by choosing finishes that stabilise colour or by embracing the natural aging process as part of the design [2]. Understanding the long-term weathering process of acetylated wood can highlight its environmental benefits, such as a reduced need for chemical treatments and lower replacement frequency. Acetylated wood might be considered a sustainable option for construction and design, supporting green building certifications and eco-friendly practices. Empirical data on the performance of acetylated wood under natural weathering can support compliance with building codes and standards [34]. In summary, experimental findings on naturally weathered acetylated wood provide a comprehensive understanding of its long-term performance, which directly influences its practical applications by enhancing design strategies, maintenance planning, product development, market acceptance, and overall sustainability.

## 4. Conclusions

The performance of acetylated alder, beech, and radiata pine exposed to 15 months of weathering was assessed with the measurement of colour, gloss, 3D roughness, wettability, infrared spectroscopy, and thermal decomposition. A relatively short period of exposure altered the appearance of the acetylated samples expressed as a change in the colour, a decrease in gloss, and an increase in roughness. Characterisation revealed changes in weathering behaviour between the investigated species. An increase in the surface roughness observed for both hardwoods was associated with the erosion of the wood surface and the leaching of photodegraded chemical components. On the contrary, values of Sa remained relatively constant for acetylated radiata pine. Acetylated pine wood exhibited lower susceptibility to bleaching at 3 months and represented a more constant *CIE L** compared to investigated hardwood species. The contact angle measured with water gradually decreased in the case of acetylated radiata pine for up to six months, then it plateaued with a slight oscillation around 15°. For both hardwood species, the big drop was observed after three months, followed by rather similar values. The PCA of IR spectra also highlighted different mechanisms in the weathering of acetylated softwood and hardwood. Scores of weathered acetylated radiata pine were located far from the others separated by PC1. Similarly, the spectra of weathered acetylated pine differed from other acetylated species, particularly in bands related to lignin, hydrogen-bonded absorbed water, and conjugated carbonyls. The acetylated hardwood samples showed higher thermal stability than acetylated radiata pine, with a maximum rate of weight loss of around 353 °C for

acetylated alder and beech and 347 °C for acetylated pine. The experimental findings provide a comprehensive understanding of the long-term performance of acetylated wood, which directly influences its practical applications by enhancing design strategies, maintenance planning, product development, market acceptance, and overall sustainability. The differences 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. The performed tests show the potential of underutilised hardwood species enhanced by the acetylation process to serve as cladding materials as an alternative to commonly utilised softwood.

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**Data Availability Statement:** The dataset used for the analysis in this study is available at Zenodo.org Open Access depository https://zenodo.org/records/11205923 deposited on 16 May 2024 [55].

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